AD-A258 035

July 1991

Final Report 1 May 1991 - 30 April 1992

16th International Conference on Defects in Semiconductors

G AFOSR-91-0217

PR 2305/C1

M. Stavola and G. DeLeo

Lehigh University
526 Brodhead Ave.
Bethlehem, PA 18015

LEHIGH-429054

AFOSR-TR- 92 0147

AFOSR/NE
Building 410
Bolling AFB, DC 20332-6448

This special final report consists of the abstracts from the 16th International Conference on Defects in Semiconductors

UNLIMITED/UNCLASSIFIED

This report consists of the abstracts for the 16th International Conference on Defects in Semiconductors held at Lehigh University, Bethlehem, PA on July 22-26, 1991. Approximately 250 papers were presented. This meeting addressed the fundamental science of imperfection in semiconductor materials. A wide range of defects of both fundamental and technological interest that include native defects, impurities, dislocations, and defects at surfaces and interfaces in a variety of semiconductor materials (Si, Ge, diamond, III-V and II-VI compounds, and related alloys) were discussed. Properties of interest included defect structures (atomic and electronic), defect introduction, reactions, motion, electrical and optical characteristics, etc.

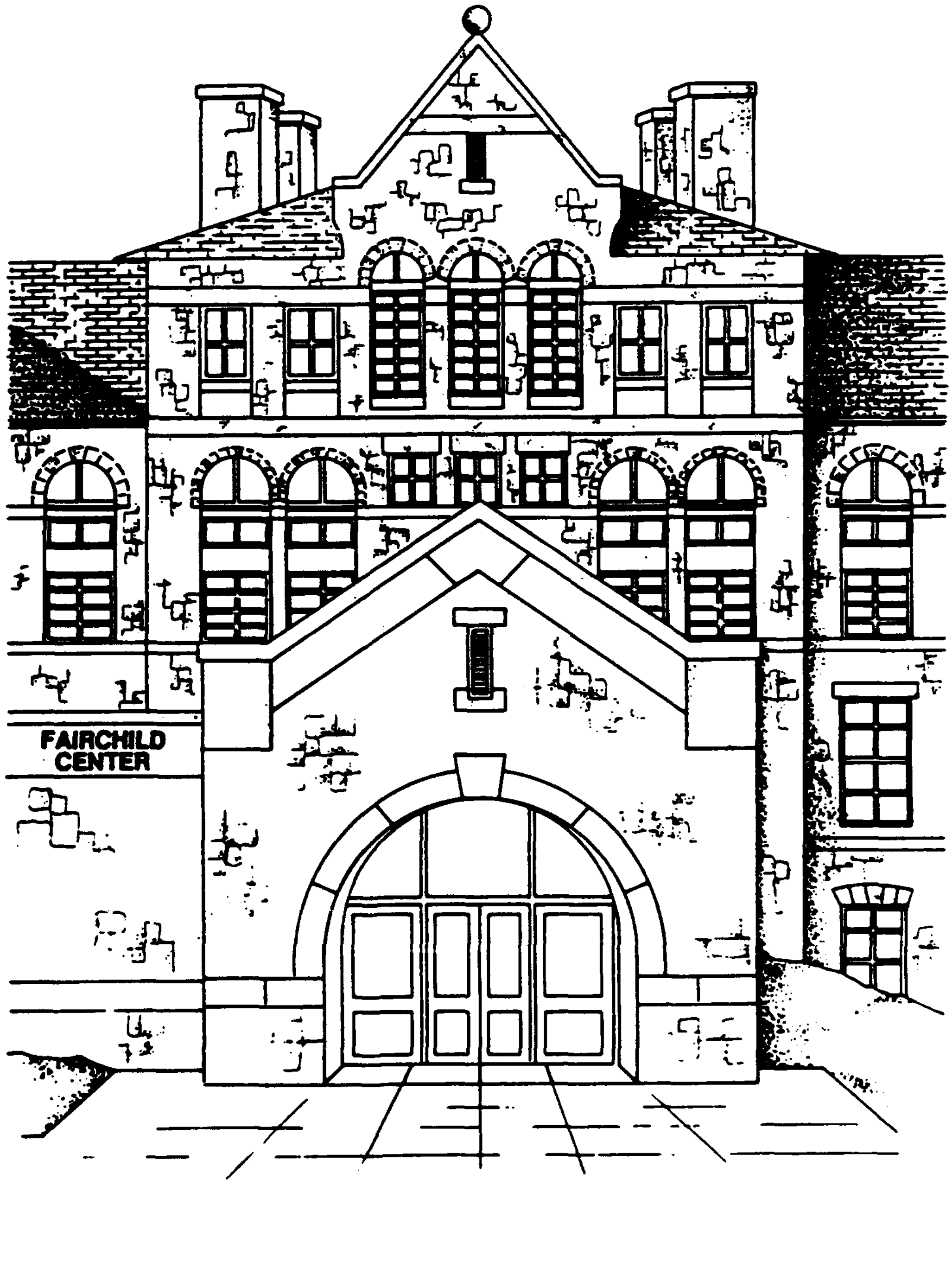
The following are a few examples of recent work that is breaking new ground in the field: (i) Oxygen in GaAs has been identified recently and has metastable characteristics. (ii) After many years of effort, there has been progress in the doping of II-VI materials. (iii) New theoretical techniques such as molecular dynamics are providing new insight into the motions of defects. (iv) Experimental techniques that involve nuclear physics and radioactive probe atoms are providing new structural information. (v) Powerful new microscopies are revealing novel structural data about surfaces and interfaces.

Defects in Semiconductors, Impurities, Irradiation Damage, Dislocations, Surface Defects, Semiconductor characterization

327

UNCLASSIFIED UNCLASSIFIED UNCLASSIFIED

16th International Conference on DEFECTS IN SEMICONDUCTORS



16th International Conference

on

DEFECTS IN SEMICONDUCTORS

Lehigh University

Bethlehem, Pennsylvania, USA

22–26 July 1991

ICDS - 16 SPONSORS

Air Force Office of Scientific Research

Bandgap Technology Corporation

Defense Advanced Research Projects Agency

Eastman Kodak Company

Ford Motor Company

Fujitsu Laboratories Ltd.

IBM

Kawasaki Steel Corporation

Lehigh University

Mobil Solar Energy Corporation

NEC Research Institute

Philips Laboratories

Rome Air Defense Center,
Solid State Sciences Directorate

Sematech

Sherman Fairchild Endowment

Solar Energy Research Institute

Sumitomo Electric Industries, Ltd.

United States Army Research Office

United States Navy Office of Naval Research

Wright Laboratory Materials Directorate

Xerox Corporation

ICDS - 16 COMMITTEES

International Advisory Committee

R.N. Bhargava, U.S.A.
J.C. Bourgoin, France
J.W. Corbett, U.S.A.
G.G. DeLeo, U.S.A.
G. Ferenczi, Hungary
H.G. Grimmeiss, Sweden
E.E. Haller, U.S.A.
L.C. Kimerling, U.S.A.
H. Kukimoto, Japan
J.M. Langer, Poland
M. Lannoo, France
J.R. Leite, Brazil
R.C. Newman, U.K.
S.T. Pantelides, U.S.A.
G.-G. Qin, P.R. China
H.J. Queisser, F.R.G.
M.K. Sheinkman, U.S.S.R.
M. Stavola, U.S.A.
A.M. Stoneham, U.K.
K. Sumino, Japan
G.D. Watkins, U.S.A.
E.R. Weber, U.S.A.

Program Committee

G.A. Baraff, U.S.A.
S.G. Bishop, U.S.A.
B. Clerjaud, France
G. Davies, U.K.
G.G. DeLeo, U.S.A.
R.J. Jaccodine, U.S.A.
H. Kukimoto, Japan
J.M. Langer, Poland
P.M. Mooney, U.S.A.
S.T. Pantelides, U.S.A.
P.M. Petroff, U.S.A.
M. Stavola, U.S.A.
G.D. Watkins, U.S.A.
E.R. Weber, U.S.A.

Local Organizing Committee

M. Stavola, co-chair
G.G. DeLeo, co-chair
B.W. Benson
W.B. Fowler
S.J. Pearton
G.D. Watkins

ICDS - 16 EPITOME

ORAL SESSIONS

Monday Morning, 22 July

	9:00	**Opening Remarks**

Session A: Plenary Session
Packard Auditorium

A 1	9:15	**Ab-initio molecular dynamics of semiconductor defects** *R. Car (Invited)*
	10:00	**BREAK**
A 2	10:30	**Impurity-induced metastabilities in semiconductors** *D.J. Chadi (Invited)*
A 3	11:15	**Atomic defect configurations identified by nuclear techniques** *T. Wichert (Invited)*

Monday Afternoon, 22 July

Session B: Oxygen in GaAs and Si
Physics Auditorium

B 1	2:00	**Electrically Active Oxygen in GaAs** *H.Ch. Alt (Invited)*
B 2	2:30	**Oxygen related point defects in GaAs** *M. Skowronski (Invited)*
B 3	3:00	**Local mode spectroscopy of OH complexes in semi-insulating gallium asenide** *B. Pajot and C. Song*
	3:20	**BREAK**
B 4	3:50	**Oxygen migration and aggregation in silicon** *M. Needels, J.D. Joannopoulos, Y. Bar-Yam and S.T. Pantelides (Invited)*

B 5 4:20 **Theoretical studies on the structure for the core of oxygen thermal donors in silicon**
P. Deak and M. Heinrich

B 6 4:40 **Reorientation of stress induced alignment of thermal double donors in silicon**
P. Wagner, J. Hage, J. Trombetta and G.D. Watkins

B 7 5:00 **Measurements of the diffusion coefficient of hydrogen in silicon monitored by catalysed enhanced oxygen diffusion jumps**
R.C. Newman, J.H. Tucker and S.A. McQuaid

Session C: Metal Impurities in Compound Semiconductors

Perella Auditorium

C 1 2:00 **Spectroscopic investigation of the Er site in GaAs:Er**
P.B. Klein, F.G. Moore and H.B. Dietrich

C 2 2:20 **Excitation mechanism of 4f emissions of Er in GaAs**
J.E. Colon, D. Elsaesser, Y.K. Yeo, R.L. Hengehold and G.S. Pomrenke

C 3 2:40 **Energy transfer in rare earth-doped III-V semiconductors**
K. Takahei (Invited)

3:10 **BREAK**

C 4 3:40 **FTIR high resolution optical study of GaAs:Fe**
K. Pressel, G. Ruckert, A. Dornen and K. Thonke

C 5 4:00 **Interstitial and substitutional Mn in GaAs: magnetic resonance studies**
S.J.C.H.M. Van Gisbergen, A.A. Ezhevskii, M. Godlewski, T. Gregorkiewicz and C.A.J. Ammerlaan

C 6 4:20 **Semi-insulating InP:Cu**
R.P. Leon, Z. Liliental-Weber, K.M. Yu, M. Kaminska and E.R. Weber

C 7 4:40 **Optical and spin dependent investigations of Mn^{2+} and V^{3+} in GaP**
P. Omling and B.K. Meyer

Tuesday Morning, 23 July

Session D: Defects in Elemental Hosts

Perella Auditorium

D 1	9:00	**In situ HVEM study of dopant dependent defect generation in silicon during 1 MeV electron irradiation** *A. Romano-Rodriguez and J. Vanhellemont*
D 2	9:20	**Atomic structures of electron-irradiation-induced defects in Si and Ge studied by TED and HRTEM** *S. Takeda, M. Hirata and S. Muto*
D 3	9:40	**Interactions between defects during the annealing of crystalline silicon** *G. Davies, K.T. Kun and T. Reade*
D 4	10:00	**An effect of the beam current and energy of fast electrons on the production rate of A-centres and divacancies in n-Si** *V.V. Emtsev, P.M. Klinger and T.V. Mashovets*
	10:20	**BREAK**
D 5	10:50	**Magnetic resonance from a metastable sulfur-pair-related complex defect in silicon** *W.M. Chen, M. Singh, A. Henry, E. Janzen, B. Monemar, A.M. Frens, J. Schmidt, K.J. Reeson and R.M. Gwilliam*
D 6	11:10	**Piezospectroscopy of two beryllium related double acceptors in silicon** *J.N. Heyman, E.E. Haller and A. Giesekus*
D 7	11:30	**On the determination of nitrogen in Czochralski silicon** *M.W. Qi, T.S. Shi, S.S. Tan, B. Zhu, P.X. Cai, W.F. Gu, D.L. Que and L.B. Li*
D 8	11:50	**The pseudo-donor electronic states of a metastable defect in silicon studied by uniaxial stress spectroscopy** *J.H. Svensson, E. Janzen, O. Kordina and B. Monemar*

Session E: Defects in III-V Semiconductors

Physics Auditorium

E 1	9:00	**Electrical activity and diffusion of shallow acceptors in III-V semiconductors** *W. Walukiewicz, K.M. Yu, L. Chan, J. Jaklevic and E.E. Haller*
E 2	9:20	**Point defects and their reactions in SI GaAs after low temperature e^--irradiation** *A. Pillukat, P. Ehrhart and W. Schilling*
E 3	9:40	**Photoluminescence related to Si_{Ga}-Si_{As} pairs in GaAs** *M. Suezawa, A. Kasuya, Y. Nishina and K. Sumino*
E 4	10:00	**EPR observation of a deep center with a p^1 electron configuration in GaAs** *U. Kaufmann, M. Baeumler and G. Hendorfer*
	10:20	**BREAK**
E 5	10:40	**Low temperature GaAs: electrical and optical properties** *M. Kaminska and E. Weber (Invited)*
E 6	11:10	**EPR of anion- and kation-antisite-defects in plastically deformed GaAs and GaP** *J. Kruger and H. Alexander*
E 7	11:30	**Uniaxial stress and Zeeman splitting studies of EL2-related photoluminescence in GaAs** *M.K. Nissen, A. Villemaire and M.L.W. Thewalt*
E 8	11:50	**Generation of anion antisite related defects in n-type InP studied by optically detected EPR and ENDOR** *H. Sun, H.P. Gislason and G.D. Watkins*

Tuesday Afternoon, 23 July

Session F: Metal Impurities in Elemental Hosts

Physics Auditorium

F 1	2:00	**Spectroscopy on transition-metal defects in silicon** *M. Kleverman, A. Thilderkvist, G. Grossman and H.G. Grimmeiss (Invited)*

F 2 2:30 **Dopant enhancement of the 1.54 um emission of erbium implanted in silicon**
J. Michel, J.L. Benton, D.J. Eaglesham, R.F. Ferrante, E.A. Fitzgerald, D.C. Jacobson, L.C. Kimerling, J.M. Poate and Y.-H. Xie

F 3 2:50 **Theory of rare-earth impurities in semiconductors**
C. Delerue and M. Lannoo

3:10 **BREAK**

F 4 3:40 **An EPR investigation of the chromium-indium defect in silicon**
P. Emanuelsson, P. Omling, H.G. Grimmeiss, W. Gehlhoff and J. Kreissl

F 5 4:00 **Theoretical interpretation of EPR measurements on the iron-shallow acceptor pairs in silicon**
L.V.C. Assali and J.R. Leite

F 6 4:20 **On the motion of iron in silicon at moderate temperature: charge state effect**
T. Heiser, A. Mesli and N. Amroun

F 7 4:40 **A study of gold-tracer diffusion in a-Si and its significance in revealing the diffusion mechanisms of transition metals in amorphous semiconductors**
W. Frank, W. Gustin, S. Coffa, J.M. Poate and D.C. Jacobson

Session G: Processing Defects and Defects in Devices
Perella Auditorium

G 1 2:00 **Interstitial defect reactions in reactive ion etched silicon**
J.L. Benton, J. Michel, L.C. Kimerling, B.E. Weir, D.J. Eaglesham, L.C. Feldman and R.A. Gottscho

G 2 2:20 **Removal of implantation damage in Cd and In doped InP and GaAs**
W. Pfeiffer, M. Deicher, R. Keller, R. Magerle, P. Pross, H. Skudlik, R. Kalish, N. Moriya, Th. Wichert and H. Wolf

G 3 2:40 **A flux analysis of point defects during SiO_2 precipitation in silicon**
W.J. Taylor, U.M. Gosele and T.Y. Tan

G 4	3:00	**Deep states associated with copper decorated oxidation induced stacking faults in Si** *M. Kaniewska, J. Kaniewski and A.R. Peaker*
	3:20	**BREAK**
G 5	3:50	**The properties of individual Si/SiO_2 defects and their link to 1/F noise** *M. Uren (Invited)*
G 6	4:20	**Hydrogen induced defects and defect passivation in silicon solar cells** *B.L. Sopori*
G 7	4:40	**Defects and Schottky barrier formation: a positive proof for epitaxial Al on AlGaAs Schottky diodes** *J.M. Langer and P. Revva*
G 8	5:00	**Recombination-enhanced diffusion of Be in GaAs** *M. Uematsu and K. Wada*

Wednesday Morning, 24 July

Session H: Donors in Compound Semiconductors - I

Physics Auditorium

H 1	8:30	**Defect metastability in III-V Compounds** *M. Scheffler (Invited)*
H 2	9:00	**High pressure studies of electronic states with small lattice relaxation of DX centres in GaAs** *J.E. Dmochowski, P.D. Wang and R.A. Stradling*
H 3	9:20	**Vibrational mode Fourier transform spectroscopy with a diamond anvil cell: modes of the Si DX center and S-related complexes in GaAs** *J.A. Wolk, E.E. Haller, M.B. Kruger, R. Jeanloz, J.N. Heyman and W.W. Walukiewicz*
	9:40	**BREAK**

H 4 10:00 **ODMR studies of donor states in $Al_xGa_{1-x}As$ ($x \geq 0.35$) doped with group-IV and group-VI impurities**
E.R. Glaser and T.A. Kennedy (Invited)

H 5 10:30 **Coexistence of deep and shallow paramagnetic excited states of the DX center in GaAlAs**
H.J. von Bardeleben, M. Sheinkmann, C. Delerue and M. Lannoo

H 6 10:50 **Magnetic resonance of x-point shallow donors in AlSb:Te bulk crystals and undoped AlSb MBE layers**
W. Wilkening, U. Kaufmann, J. Schneider, E. Schonherr, E.R. Glaser, B.V. Shanabrook, J.B. Waterman and R.J. Wagner

H 7 11:10 **Photoconductivity saturation of AlGaAs:Si evidence for negative U**
W. Jantsch, Z. Wilamowski and G. Ostermayer

Session I: Wide Band-Gap Materials

Perella Auditorium

I 1 8:30 **Photoluminescence excitation spectroscopy of cubic SiC grown by chemical vapor deposition on Si substrates**
J.A. Freitas, Jr., P.B. Klein and S.G. Bishop

I 2 8:50 **Paramagnetic defects in SiC based materials**
O. Chauvet, L. Zuppiroli, I. Solomon, Y.C. Wang and R.F. Davis

I 3 9:10 **Transition metals in silicon carbide**
J. Schneider (Invited)

9:40 **BREAK**

I 4 10:00 **Impurity-defect reactions in ion-implanted diamond**
A.A. Gippius

I 5 10:20 **ODMR investigations of the A-centres in CdTe**
D.M. Hofmann, P. Omling, H.G. Grimmeiss, B.K. Meyer, D. Sinerius and K.W. Benz

I 6 10:40 Picosecond energy transfer between excitons and defects in II-VI semiconductors
I. Broser, A. Hoffmann, C. Fricke and R. Heitz

I 7 11:00 Native defect compensation in wide-band-gap semiconductors
D.B. Laks, C.G. Van de Walle, G.F. Neumark and S.T. Pantelides (Invited)

Wednesday Afternoon, 24 July
No Sessions

Thursday Morning, 25 July

Session J: Donors in Compound Semiconductors – II
Physics Auditorium

J 1 9:00 Correlation effects due to ionized defects in semiconductors
Z. Wilamowski, W. Jantsch, G. Ostermayer and J. Kossut (Invited)

J 2 9:30 Capture kinetics of the individual DX center levels
Z. Su and J.W. Farmer

J 3 9:50 On the kinetics of photoconductivity in AlGaAs:Si
G. Brunthaler, G. Ostermayer, A. Falk, W. Jantsch and Z. Wilamowski

10:10 BREAK

Session K: EL2
Physics Auditorium

K 1 10:40 Photoquenching and photorecovery of the EL2 defect in n-GaAs under hydrostatic pressure
P. Dreszer and M. Baj

K 2 11:00 Interaction of EL2 in semiinsulating GaAs with above bandgap light
K. Khachaturyan, E.R. Weber, J. Horigan and W. Ford

K 3 11:20 **The isolated arsenic antisite defect and EL2 - an ODMR investigation of electron irradiated GaAs**
K. Krambrock, H. Sothe and J.-M. Spaeth

K 4 11:40 **Theory of the optical absorption and of the magnetic circular dichroism of antisite related defects in GaAs**
M. Lannoo, C. Delerue and G. Allan (Invited)

Session L: Hydrogen in Silicon
Perella Auditorium

L 1 9:00 **Reorientation of the B-H complex in Si by anelastic relaxation experiments**
G. Cannelli, R. Cantelli, M. Capizzi, F. Cordero, A. Frova and A. Lo Presti

L 2 9:20 **Localized kinetics of hydrogen in Cd-H complexes in silicon**
M. Gebhard, B. Vogt and W. Witthuhn

L 3 9:40 **Microstructure of hydrogen and dopants in amorphous Si**
J.B. Boyce (Invited)

10:10 **BREAK**

L 4 10:40 **Dissociation and diffusion of hydrogen in boron doped silicon**
J. Weber and T. Zundel

L 5 11:00 **New traps for interstitial hydrogen in boron- and phosphorus-doped silicon**
L. Korpas, J.W. Corbett and S.K. Estreicher

L 6 11:20 **Hydrogen-induced platelets in silicon: separation of nucleation and growth**
N.M. Johnson, C. Herring, C. Doland, F. Ponce, J. Walker and G. Anderson

L 7 11:40 **An isothermal pumping mechanism for the introduction of high hydrogen concentrations in p^+ layers in silicon**
A.D. Marwick, G.S. Oehrlein and M. Wittmer

Thursday Afternoon, 25 July

Session M: Theory
Perella Auditorium

M 1 2:00 **Pressure dependence of formation and migration enthalpies for atomic diffusion in Si: conjugate gradient minimization of total energy**
O. Sugino and A. Oshiyama

M 2 2:20 **Many-electron effects in the negative silicon vacancy**
F.G. Anderson, F.S. Ham and G. Grossman

M 3 2:40 **Structure, dynamics and stability of a-Si: an ab initio, local orbital molecular dynamics study**
D. Drabold, P. Fedders and S. Klemm

M 4 3:00 **Theory of second-order vibronic reduction factors for deep level impurities in semiconductors**
C.A. Bates, J.L. Dunn, V.Z. Polinger, L.D. Hallam, P.J. Kirk and S. Jamila

3:20 **BREAK**

Session N: New Techniques
Perella Auditorium

N 1 3:50 **Combination of DLTS and transmutation of radioactive impurities**
M. Lang, G. Pensl, M. Gebhard, N. Achtziger and M. Uhrmacher

N 2 4:10 **Microscopy of Frenkel pairs in semiconductors by nuclear techniques**
R. Sielemann, H. Hasslein, M. Brussler and H. Metzner

N 3 4:30 **Modern muon spin spectroscopic methods in semiconductor physics**
R.L. Lichti, C.D. Lamp, S.R. Kreitzman, R.F. Kiefl, J.W. Schneider, Ch. Niedermayer, K. Chow, T. Pfiz, T.L. Estle, S. Dodds, B. Hitti and R. DuVarny

N 4 4:50 **The new methods of polarized luminescence spectroscopy for the multiparticle centers in semiconductors**
S.S. Ostapenko and M.K. Sheinkman

Session O: Dislocations
Physics Auditorium

O 1 2:00 **Characterisation of dislocations in the presence of transition metal contamination**
V. Higgs, E.C. Lightowlers, C.E. Norman and P. Kightley

O 2 2:20 **Correlation of the D-band photoluminescence with spatial properties of dislocations in silicon**
K. Weronek, J. Weber, R. Buchner, M. Stefaniak, H. Alexander and F. Ernst

O 3 2:40 **Photoluminescence and electronic structure of dislocations in Ge and Si crystals**
Y.T. Rebane and Y.G. Shreter

O 4 3:00 **Characterization of point defects in Si crystals by highly spatially resolved photoluminescence**
M. Tajima, H. Takeno and T. Abe

3:20 **BREAK**

Session P: Superlattices
Physics Auditorium

P 1 3:50 **Solid state processes at the atomic level**
A. Ourmazd (Invited)

P 2 4:20 **Theory of Zn-enhanced disordering in GaAs/AlAs superlattices**
Q. Zhang, C. Wang and J. Bernholc

P 3 4:40 **Spatial partition of photocarriers trapped at deep level defects in multiple quantum well structures**
D.D. Nolte, Q. Wang and M.R. Melloch

P 4 5:00 **Dynamics of exciton capture, emission, and recombination processes at shallow donors and acceptors in center-doped AlGaAs/GaAs quantum wells**
C.I. Harris, H. Kalt, B. Monemar, J.P. Bergman, P.O. Holtz, M. Sundaram, J.L. Merz and A.C. Gossard

Friday Morning, 26 July

Session Q: Hydrogen in Compound Semiconductors

Physics Auditorium

Q 1 **9:00** **Acceptor passivation in GaP by positively charged hydrogen manifested by donor-accepted pair luminescence**
Y. Mochizuki and M. Mizuta

Q 2 **9:20** **Carbon-hydrogen interaction in III-V compounds**
B. Clerjaud, D. Cote, F. Gendron, W-S. Hahn, M. Krause, C. Porte and W. Ulrici

Q 3 **9:40** **Hydrogen-dopant interactions in III-V semiconductors**
J. Chevallier and B. Pajot (Invited)

10:10 **BREAK**

Q 4 **10:40** **Interaction of H with impurities in semiconductors**
R. Jones, S. Oberg and A. Umerski (Invited)

Q 5 **11:10** **Quantum motion of muonium in GaAs and CuCl**
J.W. Schneider, R.F. Kiefl, J.H. Brewer, K. Chow, S.R. Kreitzman, Ch. Niedermayer, T. Pfiz, T.M. Riseman, R. Kadono, S.A. Dodds, T.L. Estle, R.C. Duvarney, R.L. Lichti, C. Schwab, S.F.J. Cox, E.J. Ansaldo and E.E. Haller

Q 6 **11:30** **Effects of reverse bias annealing on hydrogenated Ti/n-GaAs Schottky barrier diodes**
S.X. Jin, M.H. Yuan, L.P. Wang, Y.Q. Jia and G.G. Qin

Q 7 **11:50** **Structure and stability of cadmium-defect complexes in III-V-compounds formed after H_2 plasma treatment**
A. Baurichter, M. Deicher, S. Deubler, D. Forkel and W. Witthuhn

Session R: Strained Layers

Perella Auditorium

R 1 **9:00** **Strain relief in thin films: can we control it?**
F.K. LeGoues (Invited)

R 2 9:30 Composition modulation effects on the generation of defects in $In_{0.55}Ga_{0.45}As$ strained layers
F. Peiro, A. Cornet, A. Herms, J.R. Morante, S. Clark and R.H. Williams

R 3 9:50 Highly non-linear chemical relaxation in strained semiconductors
F.H. Baumann, A. Ourmazd, T.Y. Chang and J.-H. Huang

10:10 BREAK

Session S: Surfaces and Low-D Structures

Perella Auditorium

S 1 10:40 O surrounding of P_b defects at the (111)Si/SiO_2 interface
A. Stesmans

S 2 11:00 Two-dimensionally localized vibrational mode due to Al atoms substituting for Ga one-monolayer in GaAs
H. Ono and T. Baba

S 3 11:20 Ab-initio study of boron delta-doped silicon
M. Schluter, M. Needels and M.S. Hybertsen

S 4 11:40 Scanning tunneling microscopy studies of semiconductor surface defects
J.E. Demuth (Invited)

POSTER SESSIONS

Tuesday Evening, 23 July, Rathbone Hall

Session PA: Donors in Compound Semiconductors

PA 1 **Laplace transform DLTS studies of the DX centers in GaSb and AlGaAs**
L. Dobaczewski, I.D. Hawkins, M. Missous, I. Poole and A.R. Peaker

PA 2 **A photoluminescence study of the charge states of a donor level in GaAs induced by hydrostatic pressure**
X. Liu, L. Samuelson and M.-E. Pistol

PA 3 **DX centers in MOCVD-grown Si-doped $Al_xGa_{1-x}As$ containing boron**
P.M. Mooney, M.A. Tischler and B.D. Parker

PA 4 **Discovery of a new metastable state of the DX center in Si doped $Al_{0.26}Ga_{0.74}As$**
P. Brunkov, A. Kommissarov, V. Evtikhiev, S. Konnikov and M. Sobolev

PA 5 **ODEPR of the deep paramagnetic state of ionized DX centers in Sn and Si doped $Al_xGa_{1-x}As$**
M. Fockele, J.-M. Spaeth, P. Gibart and H. Overhof

PA 6 **Limitations of ion channeling for the study of bistable defects**
T.N. Theis, A.D. Marwick and B.D. Parker

PA 7 **Studies of deep level transient spectroscopy of DX centers of GaAlAs:Te under uniaxial stress**
M. Li, P.Y. Yu, E.R. Weber, E. Bauser, W.L. Hansen and E.E. Haller

Session PB: Wide Band-Gap Semiconductors

PB 1 **Acceptors in silicon carbide: ODMR data**
P.G. Baranov and N.G. Romanov

PB 2 **Infrared absorption and luminescence of vanadium (V^{4+}) in silicon carbide**
A. Dornen, W. Suttrop and G. Pensl

PB 3 **Luminescence of a 4d-centre in ZnS**
R. Heitz, P. Thurian, A. Hoffmann and I. Broser

PB 4 **Theory of nitrogen and platelets in diamond**
P.R. Briddon, M.I. Heggie and R. Jones

PB 5 **Interstitial defects in II-VI semiconductors: role of the cation d states**
J.T. Schick, C.G. Morgan-Pond and J.I. Landman

PB 6 **The structure of the D-center in SiC - a study with electron nuclear double resonance**
S. Greulich-Weber, R. Muller, J.-M. Spaeth, S. Leibenzeder and R.A. Stein

PB 7 **Ferroelectric phase transitions induced by off-center impurities in narrow gap IV-VI semiconductors**
B. Vugmeister

PB 8 **PAC study of tha acceptor Li in II-VI semiconductors**
H. Wolf, Th. Krings and Th. Wichert

PB 9 **The role of vacancies in stabilizing the growth of diamond and cubic BN**
T. Lei, Y. Bar-Yam and T.D. Moustakas

Session PC: Theory

PC 1 **Donor bistability induced by electron-phonon coupling**
S. Bednarek and J. Adamowski

PC 2 **Theoretical study on the structure and properties of dislocations in semiconductors**
K. Masuda-Jindo

PC 3 **The temperature dependence of trap cross sections**
J.P. Lavine, E.K. Banghart, E.T. Nelson, W. DesJardin and B.C. Burkey

PC 4 **Lattice relaxation effects on deep levels: molecular dynamics calculations**
C.W. Myles and W.-G. Li

PC 5 **Recombination-induced defect heating and related phenomena**
I.N. Yassievich, V.N. Abakumov and A.A. Pakhomov

Session PD: New Techniques

PD 1 **ONP spectroscopy of defects in silicon**
N.T. Bagraev

PD 2 **On the analysis of digital DLTS data**
C.A.B. Ball and A.B. Conibear

PD 3 **A reevaluation of electric-field enhanced emission measurements for use in type and charge state determination of point defects**
W.R. Buchwald, H.G. Grimmeiss, F.C. Rong, N.M. Johnson, H. Pettersson and E.H. Poindexter

PD 4 **X-ray spectroscopy following neutron irradiation of semiconductor silicon**
A.J. Filo, A. Meyer, C.C. Swanson and J.P. Lavine

PD 5 **Spin dependent recombination at deep centers in Si-electrically detected magnetic resonance**
P. Christmann, M. Bernauer, A. Asenov, C. Wetzel, B.K. Meyer and A. Endros

PD 6 **Nuclear spin polarization by optical pumping**
K. Murakami, K. Hara and K. Masuda

PD 7 **Identification of band gap states in semiconductors by DLTS on radioactive isotopes**
J.W. Petersen and J. Nielsen

PD 8 **Excited defect energy states from temperature dependent ESR**
J. Schneider, C. Kisielowski, K. Maier and V. Oding

PD 9 **Muon stopping sites in semiconductors from decay-positron channeling**
H. Simmler, P. Eschle, H. Keller, W. Kundig, W. Odermatt, B.D. Patterson, I.M. Savic, J.W. Schneider, B. Stauble-Pumpin, U. Straumann and P. Truol

PD 10 **Local-mode spectroscopy and model study for assessing the role of light defects in III-V compound semiconductors**
D.N. Talwar, M.O. Manasreh, D.W. Fischer, S.J. Pearton and G. Matous

Session PE: Superlattices, Surfaces and Interfaces

PE 1 **Spectroscopy of shallow donor impurities in GaAs/AlGaAs multi-quantum wells**
J.L. Dunn, E. Pearl and C.A. Bates

PE 2 **Two electron transitions for shallow donors confined in GaAs/AlGaAs quantum wells**
P.O. Holtz, B. Monemar, M. Sundaram, J.L. Merz and A.C. Gossard

PE 3 **Localized vibrational mode absorption of silicon donors and beryllium acceptors in III-V compounds: effects of doping superlattices**
R. Addinall, R.C. Newman, A. Mohades-Kassai, M.R. Brozel, V. Mitter, D. McPhail and M.J.L. Sangster

PE 4 **Negative U systems at semiconductor surfaces**
G. Allan and M. Lannoo

PE 5 **The structure of GaAs layers grown by MBE at low temperature**
Z. Liliental-Weber

PE 6 **Ab initio calculations on effect of Ga-S bonds on passivation of GaAs surface - a proposal for new surface treatment**
T. Ohno and K. Wada

PE 7 **Differential diffractometry and TEM of InAs/GaSb/GaAs HS grown by MBE**
R.N. Kyutt, S.S. Ruvimov, T.S. Argunova, L.M. Sorokin, P.S. Kop'ev and M.E. Lutsenko

PE 8 **Structural defects in InAsSbP/InAs DH**
T.S. Argunova, R.N. Kyutt, B.A. Matveev, S.S. Ruvimov, N.M. Stus and G.N. Talalakin

PE 9 **^{17}O hyperfine study of the P_b center**
J.H. Stathis, S. Rigo, I. Trimaille and M. Crowder

PE 10 **Defects induced by high electric field stress and the trivalent silicon defects at the Si-SiO_2 interface**
D. Vuillaume and D. Goguenheim

Session PF: Alloys

PF 1 **Dopant diffusion in $Si_{0.7}Ge_{0.3}$**
D. Mathiot and J.C. Dupuy

PF 2 **Electron-trapping defects in MBE-grown relaxed $n\text{-}In_{0.05}Ga_{0.95}As$ on gallium arsenide**
A.C. Irvine, L.K. Howard and D.W. Palmer

PF 3 **Electronic structure of transition-metal impurities in $GaAs_{1-x}P_x$ alloys**
L.M.R. Scolfaro, R. Pintanel and J.R. Leite

PF 4 **Atomic ordering in (110)InGaAs and its influence on electron mobility**
O. Ueda and Y. Nakata

PF 5 **Observation of a trivalent Ge defect in oxygen implanted SiGe alloys**
M.E. Zvanut, W.E. Carlos, M.E. Twigg and R.E. Stahlbush

PF 6 **Paramagnetic resonance of Sn in AlGaAs**
M. Hoinkis, J.M. Baranowski, P. Dreszer and E.R. Weber

Session PG: Processing Defects and Defects in Devices

PG 1 **Near-surface defects introduced in n-GaAs during electron-beam deposition of Ti and Pt**
F.D. Auret, G. Myburg, W.O. Barnard, H.W. Kunert and L. Bredell

PG 2 **Ion implantation induced sheet stress due to microstructural defects in thin <100> silicon films**
J. Yuan, Z. Ling, A.J. Yencha and J.W. Corbett

PG 3 **Effects of vacancy-related defects in starting CZ Si substrate upon thermally-grown oxide breakdown field strength**
H. Koya, Y.Horioka, Y. Furukawa, T. Shingyoji, H. Suga, S. Dannefaer and S. Hahn

PG 4 **Photoluminescence characterisation of the silicon surface exposed to plasma treatment**
A. Henry, B. Monemar, J.L. Lindstrom, T.D. Bestwick and G.S. Oehrlein

PG 5 **High temperature defect-free rapid thermal annealing of III-V substrates in metallorganic controlled ambient**
A. Katz, A. Feingold, S.J. Pearton, M. Geva, S. Nakahara and E. Lane

PG 6 **Study of the gettering stability of internal oxide gettering at different levels of oxygen precipitation in Czochralski silicon**
Z. Laczik, R. Falster and G.R. Booker

PG 7 **The study of interfacial traps of InP metal-insulator-semiconductor structure**
L. Lu, J. Zhou, W. Qu and S. Zhang

PG 8 **Anomalous damage depths in low-energy ion beam processed III-V semiconductors**
S.J. Pearton, F. Ren, T.R. Fullowan, R. Kopf, W.S. Hobson, C.R. Abernathy, A. Katz, U.K. Chakrabarti and V. Swaminathan

PG 9 **A study of radiation induced defects in silicon solar cells showing improved radiation resistance**
J.W. Peters, T. Markvart and A.F.W. Willoughby

PG 10 **Role of the diffusivity of Be and C in the performance of GaAs/AlGaAs heterojunction bipolar transistors**
F. Ren, T.R. Fullowan, J. Lothian, P.W. Wisk, C.R. Abernathy, R.F. Kopf and S.J. Pearton

PG 11 **Effects of the substrate-epitaxial layer interface on the HFET and MESFET performance**
M. Spector, M.L. Gray, J.C. Licini and J.D. Yoder

PG 12 **An influence of carbon on intrinsic gettering quality and circuit performance**
L. Tesar and J. Fojtasek

PG 13 **Mobility enhanced-diffusion in electron-beam doping of semiconductors**
T. Wada, M. Takeda, Y. Shinozuka and T. Kondo

PG 14 **Electrical properties of oxidation induced stacking faults in n-type Si**
J. Kaniewski, M. Kaniewska and A.R. Peaker

Session PH: Growth Defects

PH 1 **Effect on low temperature growth on impurity and defect incorporation in AlGaAs grown by mombe**
C.R. Abernathy, S.J. Pearton, D.A. Bohling and F.A. Baiocchi

PH 2 **Characterization of GaAs/AlGaAs heterostructures grown by OMVPE using trimethylamine alane as a new aluminum source**
W.S. Hobson, S.R. McAfee, K.S. Jones, N.G. Paroskevopoulos, C.R. Abernathy, T.D. Harris, M. Lamont Schnoes and S.J. Pearton

PH 3 **Oxygen behavior during Si epitaxial growth: recent advances**
B. Pivac, A. Borghesi, M. Geddo, A. Sassella and A. Stella

PH 4 **Defects in MCZ silicon with various oxygen and carbon content**
E.P. Bochkarev, S.N. Gorin, G.N. Petrov and T.M. Tkacheva

PH 5 **Electron paramagnetic resonance studies of low temperature molecular beam epitaxial GaAs layers**
H.J. von Bardeleben, Y.Q. Jia, M.O. Manasreh, K.R. Evans and C.E. Stutz

Session PI: Late Submissions

PI 1 **DMS with Cr2+ - unusual p-d interaction**
J. Blinowski and P. Kacman

PI 2 **The exchanged-site model of DX centers**
T.N. Morgan

PI 3 **Electrical and optical properties of titanium, molybdenum and tungsten related defects in Si**
K. Schmalz, H.G. Grimmeiss, H. Pettersson, L. Tilly and K. Tittlebach

PI 4 **Stability of the positions of an interstitial impurity atom and the electronic states in semiconductors**
Y. Shinozuka

PI 5 **Effects of hydrogen in Si-doped AlAs**
E. Tuncel, H. Sigg, E. Meier, L. Pavesi, P. Giannozzi, D. Martin, F. Morier-Genoud and F.K. Reinhart

PI 6 **Influence of fluorine on electrical properties and complex formation in GaAs**
A.G. Ulyashin, Y.A. Bumay, V.E. Malakovskaya and N.V. Shlopak

Wednesday Evening, 24 July, Rathbone Hall

Session PJ: Defects in Elemental Semiconductors

PJ 1 **Implantation behaviour of ^{12}B in Si studied by beta-NMR**
B. Fischer, W. Sellinger, E. Diehl, K.-H. Ergezinger, H.-P. Frank, B. Ittermann, F. Mai, G. Welker, H.-J. Stockmann and H. Ackermann

PJ 2 **A new defect observed in annealed highly phosphorus-doped electron-irradiated silicon**
J.L. Lindstrom, B.G. Svensson and W.M. Chen

PJ 3 **Atomic configuration and instability of N and N_2 in diamond, silicon and germanium**
A. Fazzio, C.R.M. Cunha, A. Antonelli and S. Canuto

PJ 4 **Multiconfigurational C_i-P_s pair defect in silicon**
E. Gurer, B.W. Benson and G.D. Watkins

PJ 5 **Defect-impurity complex formation at high donor concentration in silicon**
A. Nylandsted Larsen and G. Weyer

PJ 6 **Photoluminescence study of aluminium-related defects in irradiated silicon**
V.A. Bykovsky, Y.I. Latushko and V.V. Petrov

PJ 7 **Observation of a configurationally unstable defect in Si**
C.A. Londos

PJ 8 **Electronic structure of isolated aluminium point defects and defect pairs in Si**
H. Overhof and G. Corradi

PJ 9 **Interaction and dynamics of high-temperature defects in carbon-rich silicon**
N.B. Urli and B. Pivac

PJ 10 **Photoluminescence of edge-defined film-fed growth silicon**
W.D. Sawyer and J. Michel

PJ 11 **Electron spin echo studies on the non-radiative triplet state of the Si-SL1 defect**
A.M. Frens and J. Schmidt

PJ 12 **Electronic structure and electric field gradient of a single Cd impurity in silicon**
S.J. Sferco, M.C.G. Passeggi and M.A. Caravaca

PJ 13 **Electron paramagnetic resonance of a multistable defect in silicon**
X. Zhan and G.D. Watkins

PJ 14 **Magneto-optical properties of Fe-Al pairs in silicon and the discovery of a new trigonal $(Fe_i-Al_s)^o$ pair**
S. Greulich-Weber, A. Gorger, J.-M. Spaeth and H. Overhof

PJ 15 **EPR studies of NTD-produced As donors in isotopically enriched ^{74}Ge single crystals**
V.S. Weiner

Session PK: H in Elemental Semiconductors

PK 1 **Hydrogen effusion in doped monocrystalline silicon - role of the surface defects on the hydrogen desorption process**
P. de Mierry, R. Rizk, J. Pesant, D. Ballutaud and M. Aucouturier

PK 2 **Effect of multiple trapping on hydrogen diffusion in silicon**
J.T. Borenstein, J.W. Corbett and S.J. Pearton

PK 3 **Evolution of hydrogen in implanted silicon**
J.W. Corbett and I.V. Verner

PK 4 **Interstitial hydrogen and {H,B}, {H,C} and {H,Si} pairs in germanium**
Dj.M. Maric, P.F. Meier and S.K. Estreicher

PK 5 **Charge states of donor-hydrogen pairs in c-Si: a fragile balance**
S.K. Estreicher, C.H. Seager and R.A. Anderson

PK 6 **Rigid rotor in a tetrahedral field: an application to (H,Be) and (D,Be) in silicon**
K.R. Martin, W.B. Fowler and G.G. DeLeo

PK 7 **Electron spin resonance study on hydrogen passivation of donors in silicon**
K. Murakami, S. Fujita and K. Masuda

PK 8 **Interaction of deuterium with internal surfaces in silicon**
S.M. Myers, D.M. Follstaedt, H.J. Stein and W.R. Wampler

PK 9 **Measurements relating to the solubility of hydrogen in silicon at high temperatures**
S.A. McQuaid, R.C. Newman and E.C. Lightowlers

PK 10 **Donor-hydrogen complexes in silicon studied by Mossbauer spectroscopy**
Z.N. Liang and L. Niesen

PK 11 **Hydrogen-assisted thermal donor depth profiles**
H.J. Stein, S.K. Hahn and P.M. Richards

PK 12 **Passivation of shallow acceptors in Si and GaAs by annealing in H_2**
I.A. Veloarisoa, D.M. Kozuch, M. Stavola, R.E. Peale, G.D. Watkins, S.J. Pearton, C.R. Abernathy and W.S. Hobson

Session PL: Metal Impurities in Elemental Semiconductors

PL 1 **Nickel related deep levels in germanium**
F.X. Zach, H. Grimmeiss and E.E. Haller

PL 2 **Electronic nature of neutral zinc in silicon: FTIR-absorption, uniaxial stress measurements**
B. Kaufmann, A. Dornen, M. Lang, G. Pensl, D. Grunebaum and N. Stolwjik

PL 3 **Vibronic interaction at a gold-related center in silicon**
S. Ghatnekar, M. Kleverman and H.G. Grimmeiss

PL 4 **The gold center in Si**
A. Thilderkvist, G.D. Watkins, M. Kleverman and H.G. Grimmeiss

PL 5 **Electronic states of Mn_4 and Fe_4 clusters in silicon**
J.R. Leite, L.V.C. Assali and A.T. Lino

PL 6 **Copper neutralization of acceptors and related defects in p-type silicon**
A. Mesli and T. Heiser

PL 7 **Diffusivities of 3d transition-metal impurities in silicon**
H. Nakashima and K. Hashimoto

Session PM: Oxygen in Semiconductors

Session PN: Defects in Compound Semiconductors

PN 1 **Combined study of complex defects in semiconductors**
P.L. Souza, C.W. Rodrigues and M.J. Caldas

PN 2 **Positron annihilation in electron irradiated gallium arsenide: atomic structure and charge states of the defects**
C. Corbel, P. Hautojarvi, F. Pierre, K. Saarinen and P. Moser

PN 3 **Defects in InP investigated by positron annihilation technique**
T. Bretagnon, S. Dannefaer and D. Kerr

PN 4 **Electrical and optical properties of GaAs doped with Li**
H.P. Gislason, I.S. Hauksson, J.T. Gudmundsson, M. Linnarsson and E. Janzen

PN 5 **Structure of 1.2 eV PL band center in GaAs:Te,Sn**
N.S. Averkiev, A.A. Gutkin, E.B. Osipov, M.A. Reshchikov, V.E. Sedov and V.R. Sosnovski

PN 6 **Localized vibrational mode resonance Raman spectroscopy of shallow impurities in GaAs**
T.D. Harris and J.K. Trautman

PN 7 **Metastable states in Si GaAs revealed by thermally stimulated current spectroscopy**
Z.-Q. Fang and D.C. Look

PN 8 **Irradiation-induced electronic levels removed in the 280K defect-annealing stage of N-GaAs**
W.O. Siyanbola, A.C. Irvine and D.W. Palmer

PN 9 **Low fluence implantations in GaAs: a Mossbauer spectroscopy investigation of individual and overlapping damage cascades**
H. Andreasen, J.W. Petersen and G. Weyer

PN 10 **Optically detected ENDOR of the $M_S=0$ state of a P_{Ga}-Y_P spin-triplet center in GaP**
H.J. Sun, F.C. Rong and G.D. Watkins

PN 11 **The gallium vacancy in p-type GaAs: an electron paramagnetic resonance study and a tight binding green function modelization**
Y.Q. Jia, H.J. von Bardeleben, D. Stievenard and C. Delerue

PN 12 **High temperature NMR study of intrinsic defects in GaAs**
W. Han, J.A. Gardner and W.W. Warren, Jr.

PN 13 **Effects of isovalent impurity doping on stoichiometry and defects in III-V semiconductors**
Yu.V. Shmartsev

Session PO: Hydrogen in Compound Semiconductors

PO 1 **Shallow and deep radiative levels of H complexes in GaAs**
M. Capizzi, C. Coluzza, V. Emiliani, P. Frankl, A. Frova and F. Sarto

PO 2 **Dissociation kinetics of hydrogen-neutralized Si donors and DX centers in GaAs and AlGaAs**
G. Roos, N.M. Johnson, C. Herring and J.S. Harris

PO 3 **Equilibrium sites and relative stability of atomic and molecular hydrogen in GaAs**
L. Pavesi and P. Giannozzi

PO 4 **Unintentional hydrogenation of III-V semiconductors during device processing**
S.J. Pearton, C.R. Abernathy, W.S. Hobson, U.K. Chakrabarti, D.M. Kozuch and M. Stavola

PO 5 **Hydrogen passivation of shallow and deep centers in GaSb**
A.Y. Polyakov, S.J. Pearton, R.G. Wilson, P. Rai-Choudhury, R.J. Hillard, W.Y. Bao, M. Stam, A.G. Milnes and T.E. Schlesinger

PO 6 **Hydrogen in InAs on GaAs heterostructures: diffusion behavior, electrical and optical effects**
B. Theys, S. Kalem, A. Lusson, J. Chevallier, C. Grattepain and M. Stutzmann

Session PP: Metal Impurities in Compound Semiconductors

PP 1 **Electrical properties of Yb, Er doped InP**
D. Seghier, T. Benyattou, G. Bremond, F. Ducroquet, G. Guillot, C. Lohmer, B. Lambert, Y. Toudic and A. Le Corre

PP 2 **Electron paramagnetic resonance identification of a trigonal Fe-S pair in GaP**
J. Kreissl, W. Ulrici and W. Gehlhoff

PP 3 **Optically detected cyclotron resonance studies of erbium and ytterbium doped InP**
M. Godlewski, B.J. Heijmink Liesert, T. Gregorkiewicz and C.A.J. Ammerlaan

PP 4 **Reinvestigation of the optical properties of the iron impurity in GaAs and InP**
A.M. Hennel, A. Wysmolek, R. Bozek, D. Cote and C. Naud

PP 5 **Photoluminescent properties of Yb doped InAsP alloys**
A.J. Neuhalfen, D.M. Williams and B.W. Wessels

Session PQ: EL2

PQ 1 **Energy level associated with the metastable state of EL2**
B. Bremond, G. Guillot, R. Azoulay, D. Stievenard, C. Delerue, S.L. Feng, M. Zazoui, H.J. von Bardeleben and J.C. Bourgoin

PQ 2 **EL2 related complex defects in semi-insulating GaAs**
U. Desnica and D. Desnica

PQ 3 **Re-examination of the configuration coordinate diagram of EL2**
D. Goguenheim, D. Stievenard and G. Guillot

PQ 4 **Vacancy in the metastable state of the EL2 defect in GaAs**
P. Hautojarvi, K. Saarinen, L. Liszkay, C. Corbel, C. LeBerre and R. Krause

PQ 5 **First-principles calculation of the pressure dependence of the transition state of EL2**
C. Ziegler and U. Scherz

ORAL SESSIONS

Session A

Plenary Session

Monday, 22 July, 9:00 AM

Packard Auditorium

Ab-Initio Molecular Dynamics of Semiconductor Defects

R. Car
Institut de Physique Appliquee, EPF - Lausanne, Switzerland

IMPURITY-INDUCED METASTABILITIES IN SEMICONDUCTORS

D. J. Chadi
NEC Research Institute
4 Independence Way, Princeton, NJ 08540

Results from recent *ab initio* total-energy calculations indicate that impurity-induced structural metastabilities may be a common phenomenon in many tetrahedrally coordinated semiconductors. Metastabilities characterized by a large-lattice-relaxation and a small formation energy are found for both covalently bonded and ionic semiconductors. Results for: P, H, and a (P+H) complex in Si, deep-donor DX centers in GaAs, and P acceptors in ZnSe are examined. Although the atomic structures of the large-lattice-relaxed (LLR) states are quite similar for all three semiconductors, there are nevertheless important differences between them. In ZnSe:P, the LLR configuration corresponds to the lowest energy state of the system and occurs for the neutral state of the acceptor. In GaAs:Si the LLR geometry is metastable and its formation requires a negatively charged state of the donor. For P-doped Si, the LLR metatstability does not occur in the absence of hydrogen. The effect of lattice relaxation on the electronic properties of impurities will also be addressed.

Atomic Defect Configurations Identified by Nuclear Techniques

Thomas Wichert

Technische Physik, Universität des Saarlandes, 6600 Saarbrücken, FRG

The impact of nuclear techniques as analytical tools for the identification of atomic defect configurations will be discussed. The strength of techniques, like perturbed $\gamma\gamma$ angular correlation (PAC), Mößbauer spectroscopy (MS), or the lattice steering effects of charged particles (channeling), is their supply of information on the chemical nature rather than on the electrical properties of a defect. Thus, nuclear techniques complement the more common electrical and optical methods which have been applied to the characterization of defects in semiconductors for a long time.

PAC and MS, like the magnetic resonance techniques, obtain their local information with respect to a probe atom via electrical or magnetic hyperfine fields that originate from the probe's microscopic surrounding. Therefore, both methods are qualified for the study of individual dopant atoms and their reactions with other defects, like impurity atoms or native lattice defects. By employing radioactive isotopes semiconductors with low dopant and defect concentrations (10^{16} cm^{-3}) can be investigated; but, at the same time, the requirement for a special nuclear decay mode limits the number of chemically different probes so that exemplary investigations rather than systematic studies are performed. Channeling experiments yield the lattice site of an individual dopant atom in a very direct way; but, the sensitivity limits the application to semiconductors containing high dopant concentrations (10^{18} to 10^{19} cm^{-3}). Again, by employing radioactive probe atoms that emit the charged particles from the dopant's site a sensitivity similar to that in PAC or MS experiments is obtained. The features of these techniques will be illustrated in the context of recent investigations of atomic defect configurations in elemental, III-V, and II-VI semiconductors.

Session B

Oxygen in GaAs and Si

Monday, 22 July, 2:00 PM

Physics Auditorium

ELECTRICALLY ACTIVE OXYGEN IN GALLIUM ARSENIDE

H. Ch. ALT*
Siemens Research Laboratories for Materials Science and Electronics
Otto-Hahn-Ring 6, D-8000 München 83, Germany

The mystery around the role of oxygen in GaAs has been solved very recently after thirty years of research. The isolated oxygen impurity occurs in GaAs in an off-center substitutional (O_{As}) and in an interstitial position (O_i). Off-center substitutional oxygen, the subject of this paper, exhibits extremely fascinating infrared-spectroscopic as well as electrical properties - both being due to a negative-U ordering of the gap levels.

Most of the results have been obtained from high-resolution Fourier transform infrared-absorption spectroscopy on commercial semi-insulating (SI) GaAs containing oxygen as a residual impurity in the concentration range of 10^{14}-10^{15} cm^{-3}. The signature of the O_{As} impurity are three sharp absorption bands due to local vibrational modes at 730.7, 714.9 and 714.2 cm^{-1} (at 10 K), corresponding to three different charge states of the defect: the zero-, one- and two-electron state, respectively. In SI samples the conversion from the high-energy band to the low-energy bands is possible by below-bandgap illumination which effects a charge-transfer process from the omnipresent deep donor EL2, being partially occupied, to the O_{As} levels.

Only the zero- and the two-electron state is observable at thermal equilibrium conditions. The one-electron state shows disproportionation into the zero- and the two-electron state - a characteristic fingerprint for a negative-U center. Therefore the one-electron state is thermodynamically unstable. This is confirmed by the activation energies of the thermal decay of the local mode bands and the threshold energies for photoionization, both giving binding energies of about 0.15 and 0.60 eV for the first and the second electron, respectively.

From a comparison with DLTS measurements on neutron-transmutation-doped samples it is concluded that the second electron level is identical with the well-known EL3 level. Very recent experiments show that rather high O_{As} concentrations are obtained by oxygen implantation. In such oxygen-implanted layers the Fermi potential is pinned by the occupancy level of the negative-U system located in the middle between the one- and the two-electron level at E_C-0.4 eV.

*Present address: Fachhochschule München, Fachbereich 06,
Postfach 200927, D-8000 München 2

OXYGEN RELATED POINT DEFECTS IN GaAs

M. SKOWRONSKI, Dept. of Metallurgical Engineering and Materials Science, Carnegie Mellon University, Pittsburgh, PA 15213

Analysis of annealing behavior and electrical properties of oxygen related point defects in GaAs is presented. It is based on Localized Vibrational Mode (LVM) absorption measurements of intentionally oxygen doped, bulk GaAs crystals.

The simplest of oxygen induced point defects in GaAs is isolated oxygen interstitial (O_i). It appears to be electrically inactive and as a consequence its infrared signature does not respond to illumination and/or doping. After prolonged annealing at temperatures above 600 °C concentration of this defect decreases to below $1x10^{15}$ cm^{-3} due to either formation of complexes with other impurities or decoration of dislocations.

Oxygen doped, as grown GaAs crystals often contain another oxygen related defect - complex of oxygen interstitial and arsenic vacancy - in about the same concentration as O_i. This center is responsible for two levels in the upper half of the energy gap. Thermal deexcitation of its optically filled levels allowed to determine their position within the bandgap. The acceptor state is located 0.55 eV below conduction band edge, while donor state activation energy is only 0.15 eV. The center, therefore, exhibits a negative-U property. Correlation of infrared absorption and DLTS measurements led to identification of center's signature as identical to that of EL3, an electron trap frequently observed in bulk GaAs. Similarly as the A center in silicon, O_i-V_{As} pair is thermally unstable and after rapid thermal annealing dissociates at temperatures above 650 °C resulting in release of oxygen interstitials. This behavior is in agreement with annealing of EL3 trap. The activation energy of dissociation was determined to be 3.8 eV. This process is not complete and small amount of O_i-V_{As} pairs is formed again by capture of vacancies during cool down. Long term annealing (T>700 °C) results is total disappearance of this center.

Infrared spectra of crystals quenched from high temperatures (T>800 °C) show evidence of new oxygen related center being created. The fine structure of its LVM signature indicates presence of oxygen bonding with two gallium neighbors. The center is electrically active, has two possible charge states and its ionization energy is 0.65 eV. Its appearance was tentatively interpreted as due to capture of V_{As}-V_{Ga} divacancy by interstitial oxygen. This center is thermally unstable and at relatively low temperatures (400 °C) undergoes series of transformations possibly leading to formation of oxygen aggregates.

At energies between 950-1200 cm^{-1} several additional lines have been observed in oxygen doped crystals. After rapid thermal annealing most of these lines disappear with concomitant increase of O_i concentration indicating their origin as due to complexes of oxygen and other impurities. Based on chemical analysis of our samples the most likely candidates are Si-O_i and Al_{Ga}-O_i pairs. The results of long term annealing and preliminary Rutherford Back Scattering and LVM absorption measurements on AlGaAs epilayers support this interpretation.

LOCAL MODE SPECTROSCOPY OF OH COMPLEXES IN SEMI-INSULATING GALLIUM ASENIDE

B. Pajot and C. Song*

Groupe de Physique des Solides, Tour 23, Université Paris 7,
2 place Jussieu, 75251 Paris Cedex 05, France

Absorption lines have been observed between 2950 and 3500 cm^{-1} at low temperature in semi-insulating GaAs samples containing oxygen. It is shown that some of these lines are due to the vibration of OH bonds in the bulk of the samples. The effect of near infrared illumination on the intensity of these lines has been studied and it is correlated with the photo-induced hole emission related with EL2 defects present in these samples. These effects are interpreted by assuming that some of the complexes involving the OH bonds are electrically active and that they can take at least two charge states. The results of piezo-spectroscopic measurements on these lines are presented and models for the OH-related complexes are discussed.

* Permanent address: Institute of Semiconductors of the Chinese Academy of Sciences, Beijing, China.

Oxygen Migration and Aggregation In Silicon,* M. NEEDELS** and J.D. JOANNOPOULOS, M.I.T., Y. BAR-YAM, Weizmann Institute of Science, and S.T. PANTELIDES, IBM T.J. Watson Research Center.- Using first-principles total energy calculations, oxygen migration and aggregation in silicon have been studied. These phenomena are more complex than hitherto believed. First, the adiabatic migration barrier of a single oxygen interstitial is found to be 1.8 +/- 0.2 eV, in marked contrast to the experimental diffusion activation energy of 2.5 eV. However, from dynamical calculations, a non-adiabatic migration barrier between 2.3 and 2.7 eV is inferred. Second, since the atomic volume per silicon atom in SiO_2 is twice the atomic volume in crystalline silicon, one would expect that oxygen aggregation would necessarily entail creation of silicon self-interstitials. However, there exist several configurations of oxygen atoms that are strongly bound even without ejecting silicon atoms from the lattice. Furthermore, the thermal treatment necessary for aggregation is identified and predictions as to how these clusters could be experimentally detected are made.

*This work was supported in part by the Office of Naval Research Grant Nos. N00014-86-K-0158 and N00014-84-C-0396.
**Present address: AT&T Bell Laboratories.

THEORETICAL STUDIES ON THE STRUCTURE FOR THE CORE OF OXYGEN THERMAL DONORS IN SILICON

Peter DEÁK*,
Max-Planck-Institut für Festkörperforschung,
P.O.Box 800665, D-7000 Stuttgart 80, FRG

Michael Heinrich,
Inst.f.Allg.Elektrotechn.u.Elektronik, TU-Wien
Gusshauss Str. 25-27., A-1040 Wien, Austria

Lawrence C. Snyder and James W. Corbett
State University of New York at Albany,
1400 Washington Ave., Albany, N.Y. 12222, USA

The series of effective mass like double thermal donors (TD) produced in heat treatments around 450 °C in oxygen-rich crystalline silicon is being studied extensively. It is generally accepted that the TD-s are defect aggregates of increasing size with a possibly common core structure containing 2-4 oxygen atoms in C_{2v} symmetry. Indirect evidence points toward the possible involvement of silicon self-interstitials in the formation of TD-s. Recently, evidence has been found for the bistability of the first two members of the series, implying similar behavior for the core.

Throughout the years, various structural models have been put forward for the core of the TD-s. Only a few have been tested by theoretical calculations and none of them could entirely account for all the features of the TD-s. We present a summary of the results obtained by applying the *same theoretical framework* to study the interaction of oxygen atoms and self-interstitials with the lattice *in a large number of cases.* We present a new model involving (at least) two oxygens and a self-interstitial in an unorthodox bonding configuration as the one best suited to explain the behavior of the first TD, including bistability and formation rate.

*Permanent address: Physical Institute of the Technical University Budapest, Hungary, H-1521

Reorientation of Stress Induced Alignment of Thermal Double Donors in Silicon

Peter WAGNER, Jürgen HAGE
Wacker-Chemitronic, P.O. Box 1140, D-8263 Burghausen, Germany
John M. TROMBETTA*), George D. WATKINS
Sherman Fairchild Lab., Lehigh University, Bethlehem, Pa. 18015, USA

Annealing of silicon containing a sufficient amount of oxygen at temperatures around 450°C generates a series of thermal double donors (TDDs) with only slightly differing binding energies. These donors can be observed by low temperature infrared absorption in two charge states. Applying uniaxial stress during the formation of TDDs induces a preferential alignment of these C_{2v}- symmetric centers /1/. The alignment is revealed by the dichroism of electronic transitions at the TDDs. It is found that the TDDs are preferentially aligned with their C_{2v} axis perpendicular to the stress direction, revealing that the TDDs exert a compressive stress on the lattice along this axis and a net tensile stress along one of the C_{2v} mirror planes. These findings are confirmed by electron spin resonance investigations /1, 2/.

Annealing such samples with preferentially aligned TDDs without applied stress again at temperatures around 450°C results in a relaxation of the alignment. Investigations of the time and temperature dependence of the reorientation provides insight into the relaxation mechanism and its activation energy. An activation energy of about 2.7 eV is observed for temperatures > 400°C for the decay of the dichroism confirmed again by electron spin resonance /2/. In the temperature region from 375 to 400°C there are indications for a reorientation of the earliest TDDs as observed with infrared absorption with a smaller activation energy (approximately 1 eV). Results relating the reorientation to the diffusion of oxygen in silicon will be presented and consequences for the TDD-models will be discussed.

*) Present address: Naval Research Lab., Washington, D.C.

1. P. Wagner, H. Gottschalk, J.M. Trombetta, G.D. Watkins, J. Appl. Physics 61 (1987) 346
2. J.M. Trombetta, G.D. Watkins, J. Hage, P. Wagner to be published

MEASUREMENTS OF THE DIFFUSION COEFFICIENT OF HYDROGEN IN SILICON MONITORED BY CATALYSED ENHANCED OXYGEN DIFFUSION JUMPS.

R.C. Newman, J.H. Tucker, S.A. McQuaid
IRC Semiconductor Materials,
Imperial College, London SW7 2BZ, U.K.

We have shown previously that there are correlated enhanced rates of formation of thermal donors and the loss of interstitial oxygen from solution in Czochralski (Cz) silicon heated in a H-plasma, rather than in a standard ambient in a furnace. It is now clear that there is enhanced long-range diffusion of O_i resulting from interactions with rapidly diffusing hydrogen atoms.

The rate of single oxygen diffusion jumps for plasma treated samples has now been monitored by the relaxation of stress-induced dichroism of the 9um IR band for anneals in the temperature range 225°C to 350°. For selected samples, the anneals were terminated after some 50% of the initial dichroism had been lost and they were then thinned from opposite sides in stages and repolished. It was thereby established that the dichroism was lost progressively from the outer layers corresponding to the diffusion depth of the hydrogen atoms. A model has been constructed for determining D_H by assuming that the dichroism is lost rapidly if $[H]>[H_{crit}]$, but otherwise the rate of loss of the dichroism is negligibly small. Some estimate of $[H_{crit}]$ is obtained for T~500°C, above which no enhancement would be expected from an extrapolation of measurements at lower temperatures. For reasonable assumptions about the numerical value of $[H_{crit}]/[H_s']$, where $[H_s']$ is the surface concentration of [H] in the plasma, we find values of D_H comparable with an extrapolation of the high temperature data of Van Wieringen and Warmoltz [1].

A Van Wieringen and N Warmoltz, Physica 22 849 (1956)

Session C

Metal Impurities in Compound Semiconductors

Monday, 22 July, 2:00 PM

Perella Auditorium

SPECTROSCOPIC INVESTIGATION OF THE Er SITE IN GaAs:Er

P.B. KLEIN, F.G. MOORE and H.B. DIETRICH
Naval Research Laboratory
Washington, DC 20375-5000, USA

The continuing interest in rare earth (RE) doped III-V semiconductors has been stimulated by the possibility of exciting the internal 4f-4f emission bands of the RE electrically to produce efficient semiconductor light emitting diodes (LED's) or lasers with thermally stable emission wavelengths. The Er^{3+} center ($4f^{11}$ configuration) is of particular technological interest, as the $^4I_{13/2}$ to $^4I_{15/2}$ emission at 1.54 μm is coincident with the low loss region of silica-based optical fibers.

Electroluminescence from GaAs:Er LED's has been demonstrated from devices grown by MBE, OMCVD and ion implantation, although none of these studies has reported optical efficiencies high enough for actual device applications. Many of the characteristics of the Er^{3+} center that have a direct bearing on the optical efficiency, such as the lattice site, equilibrium charge state and mechanism of the 4f emission, are still not well understood. In the present work, a better understanding of these properties of the Er center is obtained from measurements of Er^{3+} photoluminescence (PL), time-resolved photoluminescence and Er^{3+} electron paramagnetic resonance (EPR) from a series of Er implanted samples, as well as from samples prepared by MBE.

The dependence upon anneal temperature of the 1.54μm Er^{3+} PL spectra of Er-implanted samples annealed between 600 and 875°C indicates that several distinguishable Er sites contribute to these complex spectra. These are decomposed to yield spectra characteristic of each of the individual sites. In addition, Er^{3+} EPR measurements show that the Er^{3+} concentration exhibits a dependence upon anneal temperature that is *opposite* to that observed for the Er^{3+} PL intensity. This suggests a mechanism of excitation of the PL that does not involve Er initially in its emitting Er^{3+} state ($4f^{11}$), but rather in the Er^{2+} ($4f^{12}$) state, almost certainly complexed with a nearby defect or impurity. These conclusions are verified by ***absolute*** EPR measurements of the Er^{3+} concentration, which indicate that ***less than 0.1% of the Er in these samples is in the Er^{3+} state***. If the Er emitting state is not the equilibrium state, relaxation back to equilibrium should compete with the radiative emission. Time-resolved measurements of the Er^{3+} PL exhibit the highly nonexponential decays that would be expected from this process. These results are found not to be limited to or characteristic of ion implanted materials. Some of the same sites observed in implanted samples are also seen in MBE grown materials. In addition, MBE samples exhibiting considerably ***stronger*** Er^{3+} PL than their implanted counterparts are found by EPR to have ***lower*** equilibrium Er^{3+} concentrations.

This work is supported in part by the Office of Naval Research.

EXCITATION MECHANISM OF 4f EMISSIONS OF Er in GaAs

Jose E. COLON, David ELSAESSER, Yung Kee YEO, and Robert L. HENGEHOLD
Department of Engineering Physics, Air Force Institute of Technology, Wright-Patterson AFB, OH 45433, USA
Gernot S. POMRENKE
Air Force Office of Scientific Research, Bolling AFB, Washington D.C. 20332, USA

In order to improve our understanding of the excitation mechanism of the 4f electrons of Er in GaAs, photoluminescence (PL), photoluminescence excitation (PLE), and deep level transient spectroscopy (DLTS) experiments were carried out on GaAs:Er. Room temperature implantation of Er ions was performed into SI-, n-, and p-type GaAs substrates at an energy of 1 MeV with doses ranging from $5x10^{12}$ to $5x10^{13}/cm^2$. PL studies were done from the near bandedge at 1.52 eV (~.8 μm) down to .77 eV (~1.6 μm). The strongest Er emissions were observed for samples annealed at 750 °C/15 sec using rapid thermal annealing. It was observed that the near edge emissions present in the undoped substrates were quenched in the Er-implanted GaAs samples independently of the type of conductivity of the substrate. The PLE excitation spectra were obtained by monitoring the main Er-emission line near 1.54 μm (.805 eV) while scanning the laser excitation energy across the bandgap from 1.56 to 1.24 eV using a tunable Ti-sapphire laser. A sharp and narrow 1.54 μm Er emission line was observed at the laser excitation energy of 1.512 eV, corresponding to the bound exciton recombination energy. The intensity of the 1.54 μm line gradually increases as the laser excitation energy decreases from 1.508 eV, peaking at a laser energy of ~1.48 eV. On the other hand, only a weak 1.54 μm line was excited with above-bandgap laser excitation. These results suggest that the more efficient energy transfer to the 4f ion core of Er may come from bound exciton, donor-acceptor pair, and/or free-to-bound recombination rather than free carriers. The observed strong emission of the 1.54 μm Er line, associated with a broad range of laser excitation energies from 1.508 to 1.30 eV, suggests that Er might introduce trapping levels in the bandgap which seems to play an important role in the generation of the 4f emission. Our DLTS results, which showed the presence of two hole traps in the sample at .321 and .082 eV from the valence band, also support this interpretation. The quenching of the 1.54 μm emission at a sample temperature of 160 K is believed to be closely related to the thermal ionization energy of the .082 eV trap. Apparently, when an electron-hole pair recombines at the trap, the recombination energy is transfered non-radiatively to the 4f-ion core, and subsequently the Er characteristic lines are emitted.

ENERGY TRANSFER IN RARE EARTH-DOPED III-V SEMICONDUCTORS

Kenichiro Takahei
NTT Basic Research Laboratories
3-9-11 Midoricho, Musashino-shi, Tokyo 180, Japan

There has been increasing interest in rare earth-doped III-V semiconductors in view of the sharp and temperature-stable rare earth f-shell luminescence and the possibility of its excitation by minority carrier injection. In contrast to the well studied intra-3d-shell luminescence of transition metals, intra-4f-shell luminescence of some rare earths shows little phonon coupling and retain sharply structured luminescence spectra in III-V semiconductor hosts even at elevated temperatures. This class of material is interesting not only from a practical point of view but also from an academic point of view, because we only have a poor understanding of the energy transfer mechanism between carriers in the host semiconductors and well-shielded 4f electrons of rare earths. A salient feature of these materials worth mentioning in such a study is the fact that the characteristic sharply structured luminescence spectrum of various types of rare earth centers formed in the host crystal reflect the atomic configuration around the rare earth atoms; thus, the luminescence spectra can act as an atomic probe in identifying the types of the centers.

General features of rare earth-doped III-V semiconductors were reviewed by H. Ennen and J. Schneider in the 13th ICDS (1). Since then, there have been some advances in both synthesis of the materials and understanding of the luminescence mechanism. A low solubility of rare earth atoms in III-V semiconductors has been overcome by quasi-equilibrium growth methods such as OMVPE and MBE. Electrical behavior of rare earth ions in the host as well as their optical properties were studied. Among many combinations of rare earths and host semiconductors, Yb-doped InP has been most extensively studied. It has been found that Yb substituting for In forms an electron trap below the conduction band. Auger type energy transfer from the host to the Yb f shell takes place by the capture of an electron followed by a hole at the Yb trap, and subsequent electron-hole or exciton recombination (2).

There have been a number of papers on photoluminescence observation and light emitting diodes of Er-doped semiconductors, but its luminescence mechanism is relatively unclear. This is largely due to the presence of various types of Er centers with different atomic configurations. Such difference results in different electrical behavior and excitation efficiency under minority carrier injection. A better control of the materials and a deeper understanding of the energy transfer mechanism are required for their practical application.

REFERENCES

1) H.Ennen and J.Schneider: J. Electron. Mater. 14A (1985) 115.
2) K.Takahei, A.Taguchi, H.Nakagome, K.Uwai and P.S.Whitney: J. Appl. Phys. 66 (1989) 4941.

FTIR high resolution optical study of GaAs:Fe

K. Pressel, G. Rückert, A. Dörnen
4. Physikal. Institut, Univ. Stuttgart, 7000 Stuttgart 80, Germany
K. Thonke
Abteilung Halbleiterphysik, Univ. Ulm, 7900 Ulm, Germany

Using Fourier-transform-infrared spectroscopy, we present a detailed study on a series of absorption patterns induced by electronic transitions at Fe in GaAs. The 'internal' 3d-shell no-phonon (NP) transitions at Fe^{2+} are found between 2950 cm^{-1} and 3010 cm^{-1}, followed by a Stokes phonon sideband extending up to 3400 cm^{-1}. Superimposed is a NP transition at 3057 cm^{-1}, which is introduced by a hitherto unidentified Fe-related defect [2]. A series of spectra recorded at different sample temperatures allows us to distinguish between contribution of these two defects, and to identify numerous new features in the Fe^{2+}-related sideband. This comprises several Fe specific phonon modes and electronic transitions to higher $^5T_2$ sublevels. A complete level scheme for the Fe^{2+} ^5D substates is derived.

In the region of ~ 3950 cm^{-1} we resolve a fivefold structure of excitonic origin along with a phonon sideband. At ~ 4000 cm^{-1} absorptions due to charge transfer processes from Fe^{3+} to (Fe^{2+},h) are found. These spectra closely resemble those found for InP:Fe [3,4].

A series of lines around 7050 cm^{-1} is detected, and is analyzed in terms of a transition from Fe^{3+} to the excited $^5T_2$ state of Fe^{2+}.

All the transition energies found in the absorption spectra combine perfectly to set up a common level scheme for all ^5D sublevels and their absolute position in the bandgap of GaAs.

[1] G.K. Ippolitova and E.M. Omel'yanovskii, Sov. Phys. Semic. 9 (2), p.156 (1975)
[2] P.Leyral, C.Charreaux, G.Guillot, Journal of Lum. 40/41, p.329 (1988)
[3] A.Juhl, A.Hoffmann, D.Bimberg, and H.J.Schulz, Appl.Phys.Lett. 50(18), 1292 (1987)
[4] K.Pressel, K.Thonke, and A.Dörnen, Proc. 20th ICPS, Aug. 1990 ed. E.M. Anastassakis, J.D. Joannopoulos, World Scientific, Singapore, p. 690 (1990)

INTERSTITIAL AND SUBSTITUTIONAL Mn IN GaAs: MAGNETIC RESONANCE STUDIES

S.J.C.H.M. VAN GISBERGEN, A.A. EZHEVSKII, [1] M. GODLEWSKI, [2]
T. GREGORKIEWICZ and C.A.J. AMMERLAAN
Natuurkundig Laboratorium, Universiteit van Amsterdam
Valckenierstraat 65, NL-1018 XE Amsterdam, The Netherlands

In this report we compare the magnetic resonance parameters of substitutional Mn^{2+} and interstitial Mn^{2+} in GaAs as determined by EPR/ENDOR techniques. The interstitial Mn we report here is the first observation of an interstitial transition metal impurity in a compound semiconductor. The substitutional Mn has been observed before by EPR, but further analysis by ENDOR makes it possible to compare the behavior of its half-filled 3d shell with that of interstitial Mn.

Interstitial Mn is observed by EPR in melt-doped GaAs:Mn and in neutron irradiated GaP. Both spectra are very similar. They are isotropic and centered round g=2.0001 (GaAs) and g=2.0011 (GaP). The spectra each consist of six lines of equal intensity split by hyperfine interaction with hyperfine interaction constant $A = -266.4$ MHz, which is equal for both centers. This indicates that both centers consist of a single 100% abundant I=5/2 isotope. From ENDOR measurements we could determine that S=5/2 and g_N = 10.5 MHz/T. From this follows that the isotope involved is Mn. The analysis of the hyperfine parameter indicates that the only possible model for these centers is manganese on an interstitial site of T_d-symmetry in its 2+ charge state with electron configuration $3d^5$.

Manganese in GaAs on an substitutional site with electron configuration $3d^5$ has been observed before by EPR. We performed ENDOR measurements on this center and compared the results of these measurements with the measurements on the interstitial manganese. From this comparison we are able to determine the infuence of the covalent bonds between Mn and the surrounding As atoms on the wave function of the half-filled 3d shell, and what its effect is on the various mechanisms which contribute to the hyperfine constants and on the crystal field. We show that for the interstitial Mn the wavefunction is much more localized on the Mn atom (at least 88%) than for the substitutional Mn, where a number of 80% is found. Furthermore we found the amount of 4s admixture to the wavefunction to be much higher for substitutional than for interstitial Mn. The higher delocalization also leads to a much higher crystal field splitting parameter for the substitutional Mn.

In conclusion, for the first time the different properties of a transition metal impurity on an interstitial and on a substitutional site could be compared for a compound semiconductor.

[1] permanent address: N.I. Lobachevsky State University, Gorky, USSR

[2] permanent address: Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Al. Lotnikow 32/46, Poland

Semi-Insulating InP:Cu

R.P. Leon, Z. Liliental-Weber*, K.M. Yu*, M. Kaminska[1] and E.R. Weber

Department of Materials Science, University of California, Berkeley, CA 94720

**Materials Science Division, Laurence Berkeley Laboratory, Berkeley, CA 94720*

Many studies of transition metals in III-V compounds have been stimulated by the need to obtain thermally stable semi-insulating substrates. Our recent work involving systematic Cu diffusions in InP have shown promising results for obtaining a potential alternative to InP:Fe in providing technologically important semi-insulating InP. The study described here combines electrical measurements of Cu doped InP samples with lattice site determination and structural examination of these samples.

Cu was introduced into nominally undoped (n-type , 8×10^{15}) InP samples by diffusions at temperatures ranging from 500°C to 950°C. The samples were subsequently quenched.

Resistivity and temperature dependent Hall measurements showed that InP undergoes a transition to semi-insulating behavior for diffusion temperatures exceeding 700°C. All samples that exhibited semi-insulating character had room temperature resistivities around 2×10^6 ohms cm, and an activation energy of the carrier concentration of 0.65eV. Cu diffusion at temperatures below 700°C resulted in n-type conducting samples. These samples showed properties typical for hopping conductivity, such as thermally activated mobility and conductivity.

Structural examination of InP:Cu samples diffused at high temperatures was done with Transmission Electron Microscopy (TEM). These samples showed a large concentration of spherical precipitates about 30-60 nm in diameter. Particle induced X-ray emission (PIXE) done with channeling in the <110>, <100>, and <111> directions showed a random distribution of Cu in these samples. Such a random distribution in different crystallographic directions is typically seen when precipitates are present. Thus we conclude that the precipitates found by TEM are Cu compounds. Diffraction pattern analysis indicated that the precipitates are not pure Cu. Further studies are in progress to determine the exact phase of these precipitates.

The simultaneous observation of precipitates and semi-insulating behavior indicates that the recently proposed model for semi-insulating, annealed low temperature MBE-grown GaAs layers[1] might be applicable to this system. In this model, semi-insulating behavior is suggested to result from the overlapping depletion regions surrounding metallic precipitates. The possible relevance of this model to InP:Cu suggests that the formation of semi-insulating material due to this "buried" Schottky mechanism might be of general scope. The implications of these observations for the development of a novel type of semi-insulating semiconductor materials will be discussed.

[1] A.C. Warren, J.M. Woodall, J.L. Freeouf, D. Grischkowsky, M.R. Melloch and N. Otsuka, *Appl. Phys. Lett.* 57, 1331 (1990).

---

[1] Present address: Inst. of Experimental Physics, Warsaw Univ., Hoza 69, 00-681 Warsaw, Poland

Optical and Spin Dependent Investigations of Mn^{2+} and V^{3+} in GaP

P. Omling and B.K. Meyer*
Department of Solid State Physics, University of Lund, Box 118, S-22100 Lund, Sweden
* Physikdepartment, E16, Technical University of Munich, James Franck Straße, D-8046 Garching, F.R.G.

In the wide gap II-VI compound semiconductors absorption to and emission from crystal field split excited states of Mn^{2+} are well known features. This is in contrast to most of the III-V compounds, where the Mn^{2+}- related emissions have been identified as donor acceptor recombinations. In GaP, however, the radiative emission originates from the internal transitions between the excited state, $^4T_1$, and the ground state, $^6A_1$, of Mn^{2+}. The emission properties of the $^4T_1 \rightarrow {}^6A_1$ emission are shown to be modulated by the spin-dependent recombination from the Sulfur, S, donor in GaP. The processes by which the spin resonance of S is transferred to the internal luminescence of Mn^{2+} are studied in detail using temperature dependent photoluminescence (PL), PL excitation and optically detected magnetic resonance (ODMR) and the results will be presented.

We also compare with an ODMR investigation of the $^3T_2 \rightarrow {}^3A_2$ internal luminescence of V^{3+} in GaP, the resonance consists of an isotropic signal with a g-value of $g = 1.98$. The resonance is detected as an increase of the luminescence for above band gap and valence band-to-excited state excitation, and as a decrease of the luminescence for resonant excitation within the internal $^3A_2 \rightarrow {}^3T_1$ absorption band. The data can be understood within a model where the resonance occurs in the $^3T_1$ state, but, again spin dependent recombination from the donor S might be responsible for the modulation of the emission. From PL excitation data an energy position of E_v + 0.33 eV for the V^{3+} ground state is determined.

Session D

Defects in Elemental Hosts

Tuesday, 23 July, 9:00 AM

Perella Auditorium

IN SITU HVEM STUDY OF DOPANT DEPENDENT DEFECT GENERATION IN SILICON DURING 1 MeV ELECTRON IRRADIATION

Albert Romano-Rodríguez* and Jan Vanhellemont
Interuniversity Micro-Electronics Centre (IMEC), Kapeldreef 75, B-3001 Leuven, Belgium
*Permanent address: Càtedra d'Electrònica, Universitat de Barcelona, Diagonal 647, E-08028 Barcelona, Spain

Incident electrons with energies above 140 keV are known to introduce lattice damage in silicon at room temperature. For the creation of extended lattice defects, which can be imaged using transmission electron microscopy, quite large electron fluxes and higher electron energies and/or temperatures are required. These experimental conditions can easily be obtained by in-situ electron irradiation in a high voltage transmission electron microscope (HVEM).

First results are presented of a detailed study of the in-situ generation of extended defects in silicon, during 1 MeV electron irradiation in a HVEM. The defect nucleation and growth is studied as a function of the irradiation conditions and the dopant concentration profile and type.

Both CZ and high resistivity FZ silicon substrates are used. The influence of the dopant concentration on the defect generation is studied by irradiating cross-section Si samples with shallow junctions prepared by ion implantation. In some cases the B, P or As ions are implanted through a patterned oxide or polycrystalline mask to study the influence of two dimensional dopant profiles on the irradiation induced defect generation. The electron irradiations are performed in a JEOL1250 microscope operated at 1000 kV. The temperature of irradiation is varied between 183 and 643K and the electron flux density ranges from 2 10^{18} $cm^{-2}s^{-1}$ to 2 10^{19} $cm^{-2}s^{-1}$. The defect nucleation and growth kinetics are studied by irradiating for up to 30 min. Results of electron irradiation of uniformly doped wafers are used as a reference to interpret the observations obtained on ion implanted samples.

For all dopants, the creation of a high density of extended defect is observed in a well defined dopant concentration range. In the areas doped with higher or lower concentrations (= junction area), the density of irradiation induced defects is lower than in the lowly doped silicon substrate. Some of the samples which were irradiated at 673K, received a second irradiation at room temperature, using the same electron beam settings. Annihilation of the previously created defects is observed. In some cases even the end of range defects due to the ion implantation shrink during this second electron irradiation.

Different hypotheses to explain the observed defect behaviour are explored. The most important parameters which have to be taken into account to describe the behaviour of the generated intrinsic point defects are:
- the influence of the Fermi level on the charge of the created point defects,
- the strain introduced in the silicon lattice by the presence of a high concentration of substitutional atoms with covalent radii different from that of silicon,
- the presence of high electrical fields due to the steep dopant profiles and junctions, and
- the interaction of dopant atoms with the created intrinsic point defects, which will be most important for the area close to the peak of the dopant profile.

ATOMIC STRUCTURES OF ELECTRON-IRRADIATION-INDUCED DEFECTS IN Si AND Ge STUDIED BY TED AND HRTEM

Seiji TAKEDA, Mitsuji HIRATA and Shunsuke MUTO
Department of Physics, College of General Education, Osaka University,Toyonaka, Osaka 560, Japan

An atomic model of an aggregate of self-interstitials on {113} in Si and Ge has been derived experimentally from high-resolution transmission electron microscopy (HRTEM) and transmission electron diffraction (TED)[1]. A simulated HRTEM image of the proposed model agrees well with experiment.

The aggregates of self-interstitials induced by irradiation is usually located inside of a foil specimen. Therefore, imaging and diffraction experiments of the aggregates were prevented by the surrounding perfect crystals. In the present study, in order to avoid the difficulty, perfect crystals near top and bottom surfaces of a foil are carefully removed, after electron irradiation, with Ar ion thinning.

The model is constructed by 5-, 6-, 7- and 8-membered atom rings and has no dangling bond. It is quite interesting that the model is much related to an energetically favorable structure of a {113} surface, which was discovered by M. Gibson et al.[2]. Chains of interstitials in <110> direction[3] are arranged in <332> direction and sandwiched by the two reconstructed {113} surfaces being face to face. The sandwiched interstitials constitute hexagonal bonding partially as discussed by A. Bourret[4]. Based on the analysis of the images, the arrangement of the interstitial chains are not periodic, which fact is the origin of diffuse scattering in a plan-view (<113> incidence) electron diffraction from the aggregate.

The density of self-interstitials can be quantitatively estimated to be $0.62 \times 8/(\sqrt{11}a^2)$ (a;lattice parameter) or 5.1×10^{14} cm^{-2} for the planar aggregates, which value is distinctively smaller than that estimated in the previous studies. With the model, we reach the comprehensive understanding of the growth and unfaulting process of the aggregates under irradiation.

1) Some preliminary results: S. Takeda, S. Muto and M. Hirata:Jpn. J. Appl. Phys. 29 (1990) L1698.,S. Takeda et al.:Ultramicroscopy (1991) in press, S. Takeda: Jpn. J. Appl. Phys. (1991) in press.
2) J. M. Gibson, M. L. McDonald and F. C. Unterwald: Phys. Rev. Lett. 55 (1985) 1765.
3) T. Y. Tan: Philos. Mag. A44 (1981) 101.
4) A. Bourret: Inst. Conf. Ser. No.87 (1987) 39.

INTERACTIONS BETWEEN DEFECTS DURING THE ANNEALING OF CRYSTALLINE SILICON

Gordon Davies, Kwok Tat Kun and Tim Reade

Physics Department, King's College London,
Strand, London WC2R 2LS, UK

It has long been known that radiation damage complexes in silicon may have different thermal stabilities when other impurities are present in the semiconductor. However, the annealing kinetics of radiation damage complexes in silicon are still usually determined by taking data on a very few identical samples which are simply annealed at different temperatures. In this paper we present data on the annealing of one of the most familiar defects in silicon — the di-carbon "G" center — as functions of radiation dose and carbon impurity in well-characterised float-zone samples, monitoring the di-carbon centers through their 969 meV optical absorption.

We show that the annealing of the G center proceeds by several simultaneous processes. In an idealised silicon crystal which is perfect except for its containing one G center, thermal annealing at temperature T would destroy the G center with a decay time τ :

$$\tau = \tau_o \exp(1650 \text{ meV}/kT), \quad \tau_o = 2 \times 10^{-13}\text{s}.$$

The small pre-exponential τ_o indicates that the G center is destroyed by a single atomic jump, and we show that breakup occurs by an interstitial carbon atom C_i migrating out of the G center. In silicon containing a finite concentration $[C_s]$ of substitutional carbon atoms, the C_i atoms have a finite probability p of being captured by a substitutional carbon atom and reforming a G center. The decay time is then lengthened to

$$\tau' = \tau/(1-p)$$

and we show that for $[C_s] < 2 \times 10^{17}\text{cm}^{-3}$, $p \propto [C_s]$. Additionally, the decay *rate* of the G centers is increased in proportion to the radiation dose R :

$$1/\tau = 1/\tau_i + cR,$$

and we show that the magnitude of c is consistent with the G centers being destroyed by capturing mobile atoms emitted from other radiation damage complexes. Simultaneous with these destruction processes, G centers may also be produced by a long-range migration process activated with an energy $E_g \approx 890$ meV, as C_i atoms migrate to C_s atoms.

This paper demonstrates the complexities of the annealing kinetics which must be understood if annealing is to be modelled even in lightly irradiated float-zone silicon.

AN EFFECT OF THE BEAM CURRENT AND ENERGY OF FAST ELECTRONS ON THE PRODUCTION RATE OF A-CENTRES AND DIVACANCIES IN n-Si

Vadim V. EMTSEV, Pavel M. KLINGER
and Tatyana V. MASHOVETS
A.F. Ioffe Physical-Technical Institute,
194021 Leningrad, USSR

In spite of many studies of secondary defect formation process in Si, an effect of the electron irradiation intensity on the A-centre production rate are not yet examined in a proper way though the actual experimental intensity of pulsed electron bombardment can be veried by two orders of magnitude. Nevertheless, the A-centre production rate is often used as a monitor of the introduction rate of primary defects (vacancies V and self-intrstitials I). With this aim in view we have studied the production rate of A-centres (η_A) in n-type Cz-Si (ρ=15 Ohm.cm) as a function of the beam current (J=0.02-0.5μA) as well as the pulse length and the energy of fast electrons (E_{el}=3-7 MeV). The irradiation temperature did not exceed 50°C. Under these conditions A-centres and divacancies preponderate over other radiation-induced defects and can be readily detected by their acceptor states (E_C-0.16 eV and E_C-0.23 eV, respectively).

The main results obtained are as follows.

i) The production rate of A-centres was found to be dependent on the beam current. For each chosen E_{el} the rate η_A being varied by a factor of three or four and reached a maximum at lesser J. What is more, η_A turned out to be dependent on a duty cycle of the accelerators used i e the parameters of pulsed electron beam settle η_A. An explanation is offered assuming an effect of radiation-enchanced migration of interstitial carbon, but not in terms of the intensity-dependent production rate of primary defects.

ii) A comparison of the top rate η_A with the introduction rate of primary defects for variable E_{el} shows no pronounced increase in the fraction of separated Frenkel pairs as the energy of fast electrons is increased. It strongly suggests that the mean distance between V and I in Frenkel pairs for Eel$\lesssim$7 MeV is comparable to the annihilation radius, thus leaving only a small portion of free V and I for interactions with impurities.

iii) In contrast to A-centres, the production rate of divacancies was found to be practically constant vs the beam current and it increases almost directly with the energy of fast electrons. These results invite to conclude that divacancies are produced as primary defects for the most part but not through association of two migrating vacancies.

MAGNETIC RESONANCE FROM A METASTABLE SULFUR-PAIR-RELATED COMPLEX DEFECT IN SILICON

W.M. CHEN, MANDEEP SINGH,* A. HENRY, E. JANZÉN, B. MONEMAR
Department of Physics and Measurement Technology,
Linköping University, S-581 83 Linköping, Sweden

A.M. FRENS, J. SCHMIDT
Department of Physics, Huygens Laboratory, University of Leiden, P.O. Box 9504, 2300 RA Leiden, The Netherlands

K.J. REESON and R.M. GWILLIAM
Department of Electrical and Electronic Engineering,
University of Surrey, Guildford GU2 5XH, United Kingdom

A sulfur-related complex defect in silicon,[1-4] produced in S-doped silicon after a few seconds annealing at about 800 °C followed by a rapid quenching to room temperature, has recently attracted much attention due to its interesting configurational metastability. This complex gives rise to two deep bound exciton (BE) photoluminescence (PL) emissions at low temperature at 0.968 meV (S_A) and 0.812 meV (S_B), respectively,[2] which exhibit fingerprints of conversion between the two corresponding configurations either by light ($S_A \rightarrow S_B$ at $T < 40$ K) or by thermal annealing ($S_B \rightarrow S_A$ at $T > 40$ K).[3,4] Optically detected magnetic resonance (ODMR) signals obtained in this work for these two BE's show a corresponding conversion, which enables us to reveal useful information on the electronic structure of the excited states in the neutral charge state of the complex for each configuration. The spin-triplet nature of the lowest BE state is confirmed for both BE's and the symmetry of the corresponding configurations can be determined. The unusually broad X-band ODMR linewidth is shown from a zero-field ODMR experiment to arise mainly from unresolved hyperfine (HF) structure. In zero field the HF interactions are quenched to first order leading to a narrowing in the ODMR linewidth. A transition metal impurity atom is argued to be present in the complex and responsible for the HF structures. A substitutional sulfur-pair is also believed to be involved in the complex, partly from a characteristic energy separation between the two BE transitions. The recombination process involving the two BE transitions at the complex will be discussed with the aid of a two-particle transition model. The electron spin resonance (ESR) technique is employed to reveal the ground state properties of the complex in its paramagnetic charge state including its corresponding configurational metastability. The role of shallow dopants on the formation kinetics of the complex is also investigated.

1. T.G. Brown and D.G. Hall, Appl. Phys. Lett. 49, 245 (1986).
2. D.J.S. Beckett, M.K. Nissen and M.L.W. Thewalt, Phys.Rev. B40, 9618 (1989).
3. M. Singh, E.C. Lightowlers, G. Davies, C. Jeynes and K.J. Reeson, Mat. Sc. and Eng. B4, 303 (1990).
4. A. Henry, W.M. Chen, E. Janzén and B. Monemar, Proc. 20th Int. Conf. on the Phys. of Semiconductors, Greece, Aug.6-10, 1990, ed. E.M. Anastassakis and J.D. Joannopoulos (World Scientific, Singapore, 1990) p.545.

* Permanent address: Physics Department, King's College London,Strand, London WC2R 2LS, United Kingdom.

Piezospectroscopy of Two Beryllium Related Double Acceptors in Silicon*

J. N. Heyman, E. E. Haller
University of California at Berkeley and Lawrence Berkeley Laboratory
Berkeley, California 94720

A. Giesekus
Institut Für Physik, University of Dortmund, Germany

We present a detailed study of two beryllium related defects in silicon using infrared spectroscopy combined with uniaxial stress. We have investigated the electrically active centers with ionization energies E_v+191.9 meV (Be_1) and E_v+145.8 meV (Be_2). We find that the Be_1 center posseses tetrahedral symmetry. The ground state and excited states of this system are split at zero stress. Uniaxial stress measurements indicate that the ground state of the system transforms according to the Γ_5 representation of T_d. Our data agree qualitatively with result of recent calculations of the electronic structure of the double acceptor ground state manifold in silicon [1]. We conclude that the Be_1 double acceptor is the isolated substitutional beryllium impurity.

The excitation spectrum of the Be_2 center consists of two line series. Both display line spacings equal to the acceptor effective mass excited state spacings. The series are displaced by about 2 meV. Sets of Fano resonances corresponding to each of these series are seen in the Be_2 continuum, shifted from the line series by 63.4 meV which is the energy of the zone center optical phonon in silicon. The relative intensity of the two series is constant in all samples measured. In addition, stress induced line splittings are equal for corresponding lines of the two series. These data indicate that both effective mass series arise from the same center. Stress data indicates that the center is trigonal. Our experimental results are consistent with a distorted double acceptor model in which hole-hole correlation effects are important in the ground state but may be neglected in the description of the excited states.

Finally, we have calibrated our results with transient capacitance measurements to obtain relative optical cross sections of the Be_1 and Be_2 centers. By measuring the relative concentrations of these two defects as a function of annealing condition we extract the number of beryllium atoms in the Be_2 center. We suggest that the Be_2 center consists of two beryllium atoms on nearest neighbor substitutional sites.

1. A. Giesekus, L. M. Falicov, Phys. Rev. B 42, 8975 (1990)

* Work supported by USNSF grant DMR-88-06756

ON THE DETERMINATION OF NITROGEN IN CZOCHRALSKI SILICON

M.W. Qi, T.S. Shi, S.S. Tan, B. Zhu, P.X. Cai, W.F. Gu, D.L. Que* and L.B. Li*
Shanghai Institute of Metallurgy, Academia Sinica
Shanghai 200050, China
*Semiconductor Materials Research Institute, Zhejiang University, Hangzhou 310027, China

FTIR is widely used to determine impurities concentration in silicon for its convenience and reliance. Nitrogen in silicon is known as nitrogen pair and exhibit two infrared absorption bands at 963 and 766cm^{-1}. A calibration for determination of nitrogen in FZ-Si by 963cm^{-1} band was obtained by Itoh et al at 1985 using charged particle activation analysis. But for heat-treated FZ-Si and CZ-Si, this relation was found to give underestimated value.

This work focus on quantitative determinate of nitrogen in low-carbon CZ-Si using FTIR. Three additional bands at 1026, 996 and 801cm^{-1} are observed in N-doped CZ-Si but absent in N-doped FZ-Si, probably due to a N-N-O complex as first suggested by Stein. We found that they have good correlation and similar annealing behavior. Furthermore, their intensity varies in a complementary manner with the N-N pair bands (963 and 766cm^{-1}) up to 800°C. As the intensity of N-N pair complex increase, the intensity of N-N-O complex decrease, and vice versa. It is assumed that an interstitial oxygen and a N-N pair in silicon can combine to form a N-N-O complex. Some of these N-N-O complexes already exist in the as-grown crystal, thus reducing the number of the N-N pair, and the intensity of the 963cm^{-1} band in CZ-Si. We have shown that dynamical equilibrium exists between N-N pair and N-N-O complexes below 800°C, such as (N-N)+O $\rightleftharpoons$ (N-N-O). But the increase of absorption intensity for 963cm^{-1} band is differ from the decrease of 801cm^{-1} band intensity in samples which have been heat-treatmented below 800°C. The ratio of the increase of 963cm^{-1} band to the decrease of 801cm^{-1} band is obtained to be about 1.5. So we are able to estimate the nitrogen content in CZ-Si by modify the relation suggested by Itoh as following:

$$[N] = (1.83 \pm 0.24)\times 10^{17}\times(\alpha_{963cm^{-1}}+1.5\alpha_{801cm^{-1}})\ \text{at./cm}^3$$

The second term in the relation accounts for the nitrogen in the N-N-O complex.

*The project supported by High Pure Silicon Laboratory of China.

THE PSEUDO-DONOR ELECTRONIC STATES OF A METASTABLE DEFECT IN SILICON STUDIED BY UNIAXIAL STRESS SPECTROSCOPY

J. H. Svensson*, E. Janzén, O. Kordina, and B. Monemar

Department of Physics and Measurement Technology
Linköping University
S-581 83 Linköping, SWEDEN

*Present address: Max-Planck-Institut für Festkörperforschung
Heisenbergstrasse 1, Postfach 800665
D-7000 Stuttgart 80, FRG

ABSTRACT

The effect of uniaxial stress applied in the <100>, <110>, and <111> directions on the electronic transitions to the pseudo-donor states of the metastable configuration of a defect in electron-irradiated silicon with a lowest no-phonon line at 615.0 meV has been studied with infrared (FTIR) transmission spectroscopy. This lowest no-phonon line splits in two, four, and three components when the stress is applied in the directions <100>, <110>, and <111>, respectively, consistent with a monoclinic symmetry of the metastable configuration of the defect. The stress results support the pseudo-donor model of the defect [1]. Thus the spectrum observed is interpreted as reflecting electronic transitions from a neutral ground state for the defect in the lower half of the bandgap to effective-mass-like donor s-states, perturbed by the central-cell potential of the defect, as has been reported elsewhere [1]. The stress-induced splitting of the 615.0 meV $1s(A_1)$ line, reflects transitions at defects with different orientation with respect to the stress axis. It is also found that the magnitude of this orientation-induced splitting of the lines is strongly dependent on the deviation from the EMA-positions of the corresponding final pseudo-donor s-states. When stress is applied in the <111> direction the six conduction bands are equivalently affected by the stress and states well described by EMA should not be significantly affected. It is found, however, that the 615.0 meV line is split in three lines when stress is applied in the <111> direction already at low stress as mentioned above, due to the destruction of the orientational degeneracy. At higher stress even splittings of the lines due to transitions to the more effective-mass like s-states close to the conduction band are observed. A clear correlation between the deviation from the EMA-position and the magnitude of the stress-induced splitting related to the different defect orientations is found. A large deviation results in a large orientation induced splitting. It is also concluded that this orientation induced splitting for all lines is mainly due to the excited s-states of the pseudo-donor, whereas the neutral ground state is hardly affected by the applied stress.

1. J. H. Svensson, B. Monemar, and E. Janzén, Phys. Rev. Lett. 65, 1796 (1990)

Session E

Defects in III–V Semiconductors

Tuesday, 23 July, 9:00 AM

Physics Auditorium

Electrical activity and diffusion of shallow acceptors in III-V semiconductors

W. Walukiewicz*, K.M. Yu*, L. Chan**, J. Jaklevic*, and E.E. Haller*†

*Materials Science Div., Lawrence Berkeley Laboratory, 1 Cyclotron Rd., Berkeley CA 94720
and
†Materials Science & Mineral Engineering Dept., University of California, Berkeley CA 94720
**Present address: INTEL Corp., 3065 Bowers Ave., Santa Clara CA 95051

Reduced electrical activity of donor and/or acceptor impurities in compound semiconductors has been observed and extensively studied for many years. Despite those efforts there is no general consensus on the mechanism responsible for the formation of electrically inactive impurities. We have undertaken a systematic study of this problem in GaAs and InP, two model semiconductors which show strikingly different activation efficiency of shallow acceptor impurities. Zn acceptors were introduced into both materials by high temperature diffusion. Hall effect and C-V profiles were used to measure concentration of free holes, whereas total Zn concentration and the impurity site location were determined from particle induced X-ray emission (PIXE) channeling. In GaAs all Zn atoms up to the concentration of ~ 10^{20} cm^{-3} were found to substitute Ga sites and act as acceptors. However, in InP the hole concentration saturates at a level of ~ 5×10^{18} cm^{-3} . Our measurements show that for higher concentrations, Zn atoms are incorporated on the interstitial sites or form Zn and Zn_3P_2 precipitates. The ratio of Zn atoms on interstitial sites to the Zn atoms forming precipitates depends strongly on the post-diffusion cooling rate. For a fast cooling the portion of interstitial atoms increases. This indicates that the diffusion is controlled by the ratio of interstitial to substitutional Zn atoms (I/S) and that the precipitates are formed by an aggregation of the interstitials during the cooling.

We analyze the data in terms of the amphoteric native defect model. We show that in various semiconductors the I/S ratio is determined by the location of the Fermi level measured with respect to the Fermi level stabilization energy, E_{FS}. In InP, E_{FS} is located in the upper half of the bandgap at $E_v + 1.0$ eV. Such a configuration favors the formation of interstitial donors which compensate substitutional acceptors leading to reduced acceptor activation efficiencies of high doping levels. In GaAs with $E_{FS} \cong E_v + 0.6$ eV the I/S ratio is much smaller and practically all Zn atoms are substitutional electrically active acceptors. Within the same concept we can quantitatively explain why substitutional-interstitial diffusion is much faster in InP than in GaAs. Also, the model provides the means to address the issue of impurity diffusion at semiconductor heterointerfaces. Specifically, we show that a large difference in the location of E_{FS} in InP and $In_{0.53}Ga_{0.47}As$ is a principal driving force for segregation of acceptor impurities into InGaAs. We find that at high doping levels, the acceptor concentration in InGaAs is at least an order of magnitude higher than in InP. The calculations explain the recently reported pronounced segregation of Be impurities at the InP/InGaAs interface. We will also discuss the application of the present model to the impurity activation and diffusion in other semiconductor systems.

Work supported by US DOE under Contract DE-AC03-76SF00098.

Point defects and their reactions in semiinsulating GaAs after low temperature e^-–irradiation

A. Pillukat, P. Ehrhart and W. Schilling
Institut für Festkörperforschung, Forschungszentrum Jülich
Postfach 1913, D–5170 Jülich

Wafers of semiinsulating GaAs have been irradiated at 4.6 K with 3 MeV electrons. Irradiation doses varying between $3\cdot10^{18}$ and $3\cdot10^{19}$ e^-/cm^2 ensure that the numbers of primarily produced point defects (interstitial atoms, vacancies, and antisite atoms) are much higher than the impurity level. Without intermediate warming the defect structure was investigated by X–Ray Diffraction (change of the lattice parameter, Huang diffuse scattering) and optical absorption spectroscopy (infrared absorption, and Magnetic Circular Dichroism, MCDA). These measurements were repeated after several steps of an isochronal annealing program up to 770 K. The XRD measurements give the first direct access to the structure of interstitial atoms in GaAs. After annealing at 20 K a typical value of 2 atomic volumina for the relaxation volume of Frenkel pairs is obtained, that is independent of the irradiation dose. This value is the average over the defects on both sublattices and their possible complexes. However, a separation is *possible* due to the different annealing behaviour. The total MCDA–spectra have an obvious similarity to those of the EL2–defect. However, by considering the different annealing behaviour, the different optical quenching behaviour, and the different dependencies on the measuring temperature and the magnetic field several very specific defect spectra can be separated. Hence, the most important annealing stages will be discussed
i) The dominant annealing stage between 250 K and 330 K is attributed to the recombination of Frenkel pairs on the Ga–sublattice. The involved Ga–interstitial must have been present within a configuration that is characterized by an unusually large strain field ($V^{rel}\approx3$ at.vol). In addition to a vanishing MCDA–spectrum the formation of a new defect is observed.
ii) The annealing stage between 480 K and 580 K is characterized by the recombination of Frenkel pairs on the As–sublattice. The As–interstitial is characterized by a much smaller relaxation ($V^{rel}\approx1$ at.vol) than Ga_i. In addition the typical EL2–spectrum dominates now the "quenchable" part of the MCDA, however, defect concentrations are much higher than in the as grown state.
iii) After annealing up to 770 K most of the defects have annealed, however remaining antisite defects on both sublattices seem to dominate the MCDA.

PHOTOLUMINESCENCE RELATED TO Si_{Ga}-Si_{As} PAIRS IN GaAs

M. SUEZAWA, A. KASUYA, Y. NISHINA and K. SUMINO
Institute for Materials Research, Tohoku University, Sendai 980, Japan

Si impurity is amphoteric in GaAs occupying both the Ga site (Si_{Ga}) and the As site (Si_{As}). Si_{Ga} and Si_{As} are thought to attract each other, leading to pairing or clustering of Si atoms which may give rise to interesting effects on the property of GaAs. This paper reports some feature of defects related to Si_{Ga} and Si_{As} in GaAs investigated with photoluminescence (PL) technique.

GaAs crystals doped with Si in a wide range of concentrations were annealed at various temperatures and the resultant change in PL spectrum was followed. The PL spectrum of Si-doped GaAs depends strongly on the concentration of Si both in a low energy range and near band edge, suggesting that many kinds of deep level defects are related to Si impurity. Especially peculiar is the behavior of PL lines developed by annealing in GaAs with Si concentrations of $1.0 - 2.5 \times 10^{17}$ cm^{-3}. The peak positions of some PL lines depend sensitively on the annealing temperature. Among such PL lines we investigated the nature of two PL lines at 1190 and 1330 nm which were developed due to annealing at 900 and 500°C, respectively, in detail.

To identify the defects giving rise to these two PL lines, their excitation spectra were measured as a function of the temperature. The excitation spectrum of the 1190 nm PL line at 6 K has a very sharp peak at about 1.49 eV accompanied by a broad background. The energy of the peak coincides with the energy difference of the electronic levels between Si_{Ga} and Si_{As} and decreases with increasing temperature in a same manner as the band gap energy does. Thus, we are led to the idea that the 1190 nm PL line is caused by pairs of Si_{Ga} and Si_{As} developed due to annealing at the above temperatures. The excitation spectrum of the 1330 nm PL line has two sharp peaks and a broad background. One peak shows the feature same as that of the 1190 nm PL line and is thought to be of the same origin. The other sharp peak located around 1.39 eV shows a very weak temperature dependence of the peak position in comparison with that of the first peak. We think that the agent giving rise to the PL line 1330 nm PL line is a pair of Si_{Ga} and Si_{As} coupled with some other defect. The shape of the 1190 nm PL line shows a peculiar temperature dependence which can be interpreted in terms of strong coupling of electrons and lattice.

EPR OBSERVATION OF A DEEP CENTER WITH A p^1 ELECTRON CONFIGURATION IN GaAs

U. Kaufmann, M. Baeumler and G. Hendorfer
Fraunhofer-Institut für Angewandte Festkörperphysik
Tullastraße 72, D-7800 Freiburg, Fed. Rep. Germany

A new light-induced electron-paramagnetic-resonace (EPR) spectrum, labelled FR4, has been discovered in undoped semiinsulating GaAs at temperatures below 4.2 K. The center in question has an effective ground state spin $S = 1/2$ interacting with a $\approx$ 100% abundant $I = 1/2$ nucleus. A very unusual feature of the spectrum is that its g-factor is small and isotropic, $g_{\parallel} = g_{\perp} = 0.344$ while the hyperfine parameters are large and highly anisotropic, $A_{\parallel} = 1498 \times 10^{-4} cm^{-1}$, $A_{\perp} = 253 \times 10^{-4} cm^{-1}$ and reveal trigonal symmetry. It is shown that a strongly localized p^1 electron configuration can consistently account for the spin Hamiltonian parameters and that the center likely is a neutral Tℓ "atom" (configuration $6s^2 6p^1$). To our knowledge this is the first example of a defect in a semiconductor with such an electron configuration.

LOW TEMPERATURE GaAs: ELECTRICAL AND OPTICAL PROPERTIES

Maria KAMINSKA and Eicke WEBER*
Institute of Experimental Physics, Warsaw University, Hoza 69, 00-681 Warsaw, Poland
*Department of Materials Science and Mineral Engineering and Center of Advanced Materials, Lawrence Berkeley Laboratory, University of California, Berkeley CA 94720, USA

The growth of GaAs by molecular beam epitaxy (MBE) at low (190-300 ^{o}C) substrate temperatures (often referred to as LT GaAs) was initialized three years ago at Lincoln Laboratory, MIT. Since then LT GaAs layers have gained a big interest because of their technological importance as buffer layers for GaAs integrated circuits as well as because of their unusual structural, electrical and optical features.

It has been shown that LT GaAs is As rich with about 1% more As than Ga. In spite of the high off-stoichiometry as well as the low growth temperature, the LT GaAs layers are still crystalline. However, the lattice parameter of LT GaAs increases by about 0.1% in comparison with bulk melt grown GaAs.

The dominant point defect of LT GaAs has been identified as arsenic antisite related with concentration as high as 10^{20} cm^{-3} in as grown layers. Arsenic antisite defect controls optical and electrical properties of LT GaAs. For as grown layers hopping conductivity within arsenic antisite band occurs and the near infrared absorption spectrum is dominated by EL2-like band. The features of arsenic antisite defect in LT GaAs differs in some points from EL2 defect. Especially, the metastable behaviour of arsenic antisite after illumination at low temperatures will be presented and compared with EL2.

Annealing of LT GaAs in the temperature range of 350-600 ^{o}C changes dramatically its electrical and optical properties leading to high resistivity of the layers. This annealing is associated with the substantial decrease of arsenic antisite concentration. Process of arsenic antisite creation during crystal growth, its differences from EL2, its migration and formation of arsenic precipitates during annealing in connection with electrical and optical properties of LT GaAs will be discussed in the paper.

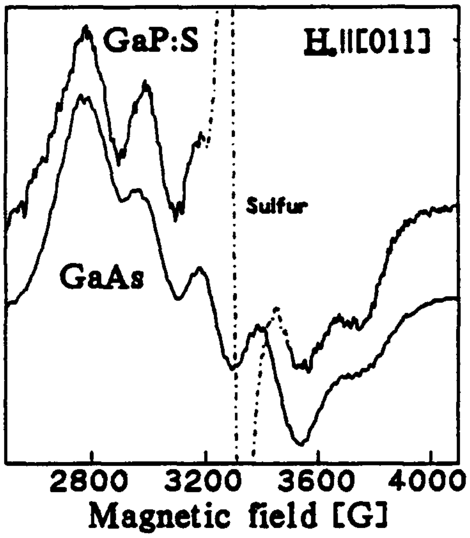
EPR of Anion - and Kation - Antisite - Defects in Plastically Deformed GaAs and GaP

J. Krüger and H. Alexander
Abteilung für Metallphysik, Universität zu Köln,
Zülpicher Str. 77, D - 5000 Köln 41

Plastic deformation of GaAs results in the generation of antisite defects /1/.

The number of the EPR centers attributed to the As_{Ga}^{+} antisite defect can be enhanced up to $10^{17}\,cm^{-3}$. Characteristic parameters as g-value and hyperfine splitting of those defects produced by plastic deformation are identical with parameters of grown-in defects. This is in clear contrast to production by irradiation with electrons and neutrons. Part of the As_{Ga}^{+} spectrum is quenchable (and, therefore, can be attributed to the metastable donor EL 2) while the remaining part cannot be quenched.

Simultaneously to the As_{Ga}^{+} spectrum another slightly anisotropic spectrum of equal intensity is created. It is clearly distinguishably from the first by its shorter spin lattice relaxation time and much lower hyperfine interaction. Since the same spectrum is also present in plastically deformed GaP /2/, Gallium can be identified as the central nucleus of the defects, in contradiction to the proposal of other authors /3/. As revealed from temperature dependence of the line shape the defect is composed of two defects of non - cubic symmetry distinguished by different superhyperfine interaction. Simulations of the spectra proved that the symmetry of one of them is at least monoclinic - I.



The same spectrum can also be detected in GaAs irradiated with thermal neutrons after bleaching of EL2. Therefore a conceivable symmetry lowering influence of dislocations in deformed samples can be ruled out.

We attribute the new signal to Ga antisite defects probably parts of larger complexes. Our hypothesis is in agreement with theoretical calculations /4/ which predict a T_2 state for the Ga antisite resulting in a symmetry lowering Jahn - Teller distortion.

/1/ M. Wattenbach, J. Krüger, C. Kisielowski - Kemmerich, H. Alexander; Mat. Sci. Forum **38 - 41**, 37 (1989)

/2/ J. Palm, C. Kisielowski - Kemmerich, H. Alexander; Appl. Phys. Lett. **58**, 68 (1991)

/3/ E. Christoffel, T. Benchiguer, A. Goltzene, C. Schwab, Wang Guangyu and Wu Ju; Phys. Rev. B **42**, 3461 (1990)

/4/ G.A. Baraff and M. Schlüter; Phys. Rev. Lett. **55**, 1327 (1985)

UNIAXIAL STRESS AND ZEEMAN SPLITTING STUDIES OF EL2-RELATED PHOTOLUMINESCENCE IN GaAs

M.K. Nissen, A. Villemaire and M.L.W. THEWALT
Department of Physics, Simon Fraser University
Burnaby, B.C., Canada V5A 1S6

The recent discovery[1] of sharp photoluminescence lines resulting from a transition from a very shallow excited state of neutral EL2 to the deep EL2 ground state has opened up exciting new possibilities for perturbation spectroscopy on this important and controversial defect. Such measurements can provide information on the defect symmetry, which continues to be a subject of dispute.

The new photoluminescence process studied here is quite distinct from the 1.039 eV no-phonon intracenter absorption line which was used for previous perturbation studies. The 1.039 eV transition connects the neutral EL2 ground state with an excited state which is resonant with the conduction band and is deduced from the piezospectroscopy of this line to have T_2 symmetry. From the absence of any structure in addition to the splittings expected for an $A_1 \rightarrow T_2$ transition (2 fold, 2 fold and 3 fold for <001>, <111> and <110> stresses), it was deduced that EL2 had T_d symmetry. However, it could be argued that the existence of these electronic splittings, together with the difficulties of achieving a high signal-to-noise ratio from the very weak 1.039 eV absorption line, had masked some small effects resulting from an EL2 symmetry lower than T_d.

The photoluminescence transition is a more promising candidate for perturbation studies. It is a very narrow line, and using Fourier transform spectroscopy, impressive signal-to-noise ratios can be achieved. More importantly, the initial state of this transition is a shallow 2S-like bound state associated with the Γ conduction band minimum. Thus the photoluminescence transition is $A_1 \rightarrow A_1$, and there will be no electronic splittings under uniaxial stress. This should enable us to observe any small splittings which would arise from a stress-induced lifting of the orientational degeneracy if EL2 did indeed have a symmetry lower than T_d.

Our results for <001>, <111> and <110> stresses up to 500 MPa show absolutely no splitting of the transition, only an identical energy shift for all three directions of stress which agrees well with the known hydrostatic shift between the EL2 ground state and the Γ condition band edge. Similarly, our Zeeman results reveal only an isotropic doublet splitting of the line resulting from the lifting of the spin degeneracy in the initial and final states. Again, the magnitude of the splitting agrees well with the known g factors of the EL2 ground state and the Γ conduction band edge.

In conclusion, our results provide no evidence for a neutral EL2 ground state symmetry lower than T_d, and thus support the isolated arsenic antisite model of the origin of this defect.

1-M.K. Nissen, T. Steiner, D.J.S. Beckett and M.L.W. Thewalt, Phys. Rev. Lett. 65,2282 (1990).

GENERATION OF ANION ANTISITE RELATED DEFECTS IN n-TYPE InP STUDIED BY OPTICALLY DETECTED EPR AND ENDOR

H. SUN, H. P. GISLASON*, R. E. PEALE, and G. D. WATKINS

Sherman Fairchild Laboratory, Lehigh University, Bethlehem PA, 18015, USA
*Science Institute, University of Iceland, Dunhaga 3, 107 Reykjavik, Iceland,

We have investigated the generation of anion antisite related defects in n-type InP by electron-irradiation with 2 MeV electrons. The irradiation gives rise to an absorption band in which a magnetic circular dichroism (MCD) signal is detected. Monitoring this MCD band an ODMR signal characteristic of the anion antisite P_{In} - is observed. Using the higher resolution of optically detected electron-nuclear-double resonance (ODENDOR) we identify the signal as the one previously observed and identified as a perturbed antisite in electron-irradiated n-type InP and p-type samples irradiated to become n-type [1]. We also find identical signals in different semi-insulating samples investigated in the present study.

The intensities of the MCD and ODMR signals in the n-type samples strongly depend on the irradiation dose. This dependence is investigated in a range of different n-type InP samples doped with Sn and Si with electron concentration in the range 5×10^{15} - 2×10^{17} cm^{-3}. The ratio between the ODMR and MCD intensities is a sensitive parameter to the electron concentration and irradiation dose. It is found that the strongest intensity ratio observed in each sample is not a simple function of the initial electron concentration, while the onset of a detectable ODMR signal critically depends on the electron fluence. The latter is deduced to be a consequence of the conductivity of the samples which prevents magnetic resonance measurements unless compensated by the irradiation [2]. These observations are used to examine the hypotheses that the electron irradiation is either revealing the paramagnetic charge state of a fixed concentration of antisite defects through the introduction of electron traps, or alternatively producing the antisite defects.

In a recent ODMR study of p-type InP the level position of the isolated P_{In} antisite was estimated from combined photoluminescence and MCD-absorption measurements [1,2]. In that case the defect was uambiguously identified by ODENDOR, which also revealed the introduction of the perturbed antisite into the p-type samples as the irradiation converted them to n-type.

We observe different relative intensities for different peaks in the complicated ODENDOR signal characteristic of the antisite signal in n-type InP. We find that the relative intensities may be changed both with irradiation dose and by illumination. We conclude from the ODENDOR signals of the n-type samples in the present investigation that there are more than one perturbed antisite present in the electron-irradiated n-type samples, a fact that complicates the analysis of the generation mechanism.

1. H.P. Gislason, H. Sun, F. Rong and G.D. Watkins, in *The Physics of Semiconductors*, Vol. 3, (World Scientific, Singapore, 1990) p. 666.
2. H.P. Gislason, H. Sun, F. Rong and G.D. Watkins, submitted to Phys. Rev. B. (1991)

This work was supported by the U.S. Office of Naval Research (Electronics and Solid State Sciences Program) under contract No. N00014-90-J-1264.

Session F

Metal Impurities in Elemental Hosts

Tuesday, 23 July, 2:00 PM

Physics Auditorium

SPECTROSCOPY ON TRANSITION-METAL DEFECTS IN SILICON.

M. Kleverman, A. Thilderkvist, G. Grossmann, and H. G. Grimmeiss
Department of Solid State. Physics, University of Lund
Box 118, S-221 00 LUND, Sweden

Defects related to transition-metal impurities (TMI's) in silicon form an interesting class of defects due to their partly filled d shells. We will here present an overview on some recent results obtained by high-resolution absorption spectroscopy using perturbation techniques i.e. uniaxial stress and Zeeman spectroscopy. The present understanding of the TMI's is mainly based on EPR and, more recently, also on theoretical investigations. However, EPR has an inherent drawback compared with spectroscopic methods in that it only applies to paramagnetic centers and then probes only the ground state(s). In Si, the TMI excitation spectra are dominated by one-particle transitions from a localized many-particle ground state to shallow donor and acceptor like states. In the final states, exchange effects between the shallow particle and the core states may be observed as e.g. for the neutral interstitial Mn impurity. This spectrum is due to transitions from the $^4T_1$ ground state to $nS(\Gamma_8)$ shallow-hole states. Exchange interaction between the $^3A_2$ core and the j=3/2 holes results in levels having a total angular momentum of 5/2, 3/2, and 1/2. The splitting of the levels decreases with n due to increasing delocalization of the hole. Another example is the neutral isolated interstitial Fe impurity which shows a donor like spectrum dominated by transitions to p-like donor states. The exchange interaction is drastically reduced compared with Mn due to the small overlap between the excited electron and the final core state. Here, three superimposed donor spectra are observed since three final states, derived from the $^4T_1$ ground-state term of Fe^+, are reached in the transitions. The Fe spectrum shows yet another interesting feature in that transitions to states derived from a $^5T_1$ term are observed. Spin unrestricted calculations show an $a_1\uparrow$ resonance close to the conduction band minima. Transitions to this $a_1\uparrow$ state will then result in a $^5T_1$ term close to the conduction band. The final example will be the single substitutional Au impurity in Si. The lack of any EPR data has long puzzled defect scientists. Recent Zeeman results have revealed detailed information on the electronic structure of neutral gold. Au is an S=1/2 center, with $g_{\parallel}$=2.8 and $g_{\perp}$=0 and has a static <100> tetragonal distortion. As in the case of the isoelectronic Pt^- center, Au shows reorientation effects between equivalent distortions even at 1.9K.

DOPANT ENHANCEMENT OF THE 1.54 μm EMISSION OF ERBIUM IMPLANTED IN SILICON

J. MICHEL*, J.L. BENTON, D.J. EAGLESHAM, R.F. FERRANTE**, E.A.FITZGERALD, D.C. JACOBSON, L.C. KIMERLING*, J.M. POATE, AND Y.-H. XIE

AT&T Bell Laboratories, Murray Hill, NJ 07974
*MIT, Department of Materials Science and Engineering, Cambridge, MA 02139
**U.S. Naval Academy, Department of Chemistry, Annapolis, MD 21402

Rare earth elements in semiconductor materials have been of special interest in recent years because their photon emission is essentially host lattice independent . Recent research has been especially focused on erbium because of its strong luminescence at 1.54 μm, which coincides with the absorption and dispersion minimum of SiO_2 optical fibers. Furthermore, the development of a strong erbium emission from erbium in silicon is a crucial step towards OEICs (optoelectronic integrated circuits) on silicon. Several recent studies have reported luminescence from erbium in silicon, but there is little knowledge concerning optimal processing parameters for the most efficient emission.

In our study we used Er-implantation (1-5MeV) into Si to achieve high concentrations to depths of 2 μm below the silicon surface. Annealing conditions were optimized and the solid solubility was determined by precipitate analysis using transmission electron microscopy. We show that the photoluminescence intensity difference of the Er emission between FZ and Cz Si is due to the presence of oxygen in Cz material. Oxygen enhances the PL intensity by approximately two orders of magnitude. Additional implantation of the light impurities C, N or F results in enhancement of the erbium emission which is even stronger than the effect of O. We show that this enhancement is directly correlated to the interaction of these impurities with erbium. Each dopant produces a unique crystal field splitting of the erbium $4f^{11}$ levels, which gives rise to separate sets of emission lines.

We have observed the erbium luminescence above room temperature in optimally processed Si. We have designed and fabricated Er-implanted LED's which routinely operate at temperatures below 240 K. We shall report the processing and the defect reactions which optimize LED performance and discuss the potential of rare earth centers in silicon for OEIC applications.

THEORY OF RARE-EARTH IMPURITIES IN SEMICONDUCTORS

Christophe DELERUE and Michel LANNOO
Laboratoire d'Etude des Surfaces et Interfaces, URA 253 CNRS
ISEN, 41, boulevard Vauban, 59046 Lille Cedex, France

Recently, rare-earth (RE) impurities in semiconductors have been attracting increasing attention [1] because of their promising applications due to sharp intra-4f-shell transitions. If luminescence properties now begin to be well understood [2], little is known about RE electrical activity and RE electronic structure. Therefore we present a model for the electronic properties of RE impurities in covalent and ionic semiconductors. Our calculation proceeds in two steps. First, we obtain the valence electronic structure using a selfonsistent Green function calculation and assuming that the 4f shell acts as a frozen core shell. Secondly, 4f transitions are examined taking in account multi-electron effects which allows to position the 4f levels with respect to the bands of the semiconductors. The comparison of our results with existing experimental data is good. In particular, we explain why in most cases there is no deep level associated with these defects, and we also correctly predict the stable state, at least in cases where experimental data are available.

REFERENCES

[1] M. Ennen and J. Schneider, Proc. 13th Int. Conf. on Defects in Semiconductors, Coronado, p. 115 (1984).
[2] R. Boyn, Phys. Stat. Sol., 148, 11, (1988).

AN ELECTRON PARAMAGNETIC RESONANCE INVESTIGATION OF THE CHROMIUM-INDIUM DEFECT IN SILICON

P. EMANUELSSON, P. OMLING and H. G. GRIMMEISS
Department of Solid State Physics, Box 118, S-221 00 Lund, Sweden
W. GEHLHOFF and J. KREISSL
Academy of Sciences, Centre for Scientific Instruments,
Rudower Chaussee 6, Berlin 1199, FRG

The transition metal-acceptor pairs in silicon have shown to be exciting objects of study. Especially the question why some but not all of them show metastable properties has motivated extensive studies. In this paper we present the EPR spectrum of the chromium-indium pair. The fine structure shows a very complicated angular dependence because the zero-field splitting and the Zeeman energy are in the same range, a so called intermediate case. Also the indium hyperfine structure is complicated because of a lot of forbidden transitions.

Both the fine and hyperfine structures are successfully analysed using a computer diagonalisation of the spin Hamiltonian. Both the trigonal and cubic fine structure interactions has to be included in order to explain the spectrum. For the hyperfine structure, the "normal" hyperfine and the quadrupole interactions are found to have comparable magnitudes, and this is the reason for the complicated structure with a lot of forbidden transitions.

The proposed model is an Cr^+ ion on the nearest interstitial position from a substitutional In^-. The spectrum is interpreted as originating in the manifold of the ^6S ground state of Cr^+ in a cubic crystal field with a trigonal distortion caused by the In^- ion.

Attempts to observe an orthorhombic CrIn pair failed, which suggests that the chromium-acceptor pairs do not show the metastable behaviour of the iron-acceptor pairs. This is supported by the previous EPR studies made on the CrB, CrAl and CrGa pairs. The difference in this respect between the Cr- and Fe-acceptor pairs might be the different electronic ground states (^6S for Cr^+ and ^4F for Fe^+). This interpretation is supported by the investigations of Mn-acceptor pairs, which have the same electronic configuration as the Cr-acceptor pairs and also show no metastability.

THEORETICAL INTERPRETATION OF EPR MEASUREMENTS ON THE IRON-SHALLOW ACCEPTOR PAIRS IN SILICON

Lucy V.C. ASSALI and José R. LEITE
Instituto de Física da Universidade de São Paulo
C.P. 20516, São Paulo, 01498 S.P., Brazil

Pairs of transition metals (TM) and group III A shallow acceptors (A) in silicon have been investigated since the pioneering work of Ludwig and Woodbury. They reported on the electron paramagnetic resonance (EPR) spectra of the trigonal Fe-B, the trigonal Fe-Ga, and the orthorhombic Fe-In complexes. The trigonal pairs display a <1 1 1> axial symmetry indicating that they may consist of substitutional acceptor with a TM atom placed at a nearest-neighbor interstitial site, and the orthorhombic pair displays a <1 0 0> symmetry consistent with the assumption that the A atom is substitutional and the TM impurity may be placed at the next-nearest-neighbor interstitial site. Recently, however, both, the <1 1 1> and <1 0 0> symmetries have been ascribed to the Fe-*Al* and Fe-Ga pairs according to EPR investigations. The bistability of the Fe-*Al*, Fe-Ga and Fe-In pairs has also been observed by deep-level transient spectroscopy (DLTS) experiments. Recently, the missing trigonal Fe-In complex was identified by EPR and a new spectrum of this pair in <1 0 0> symmetry was found and interpreted as the complex ground state.

In this work we continue our theoretical investigations on the electronic structure of these pairs. By carrying out multiple-scattering Xα molecular cluster model calculations we have shown that the ground state of the trigonal Fe-Ga pair is a low spin state (S=1/2), in agreement with EPR experiments. However, we have found that the ground state of both, the trigonal and orthorhombic, Fe-*Al* pair is a high spin state (S=3/2). According to our calculations the S=1/2 spin configuration corresponds to excited states for the Fe-B and Fe-*Al* pairs in both symmetries and for the orthorhombic Fe-Ga pair.

On the motion of iron in silicon at moderate temperature: Charge state effect

T.Heiser, A.Mesli, and N.Amroun
Laboratoire PHASE (UPR du CNRS n°292),
23, rue du Loess,67037 Strasbourg Cedex, France

Interstitial iron (Fe_i) in silicon is studied by means of capacitance measurements. We focused our attention on its behaviour during low temperature annealing (up to 450K). In particular, the precipitation of Fe_i in both, n-type and p-type silicon, were investigated and the influence of strong electric fields on the annealing kinetics were looked for. The unavoidable iron contamination of silicon wafers during processing as well as the presence of strong electric fields in operating power devices gave cause for this work.

Isothermal annealing kinetics yielded completely different results when performed on n-type or p-type silicon. First order diffusion limited precipitation kinetics, as often described in literature, were only observed in p-type material. Loss of Fe_i in n-type silicon followed a much slower annealing-time dependence. The observed iron depth distribution indicated that the loss of Fe_i in n-type silicon at moderate temperatures is limited by diffusion towards the sample surface.

The presence of strong electric fields, in the depletion region of a Schottky diode, changed considerably the behaviour of iron, despite of its neutral charge state. Enhanced loss of Fe_i occured, following a first-order kinetic in n-type material, while in p-type silicon, the kinetics were even faster. Profil measurements indicated, that the electric field drifted the iron out of the depletion region. The results could be understood in terms of an effective mobility, taking into account the statistics of electron-hole emission processes. This model involves a doping level dependence of the kinetics which was confirmed experimentally.

Finally, from Fe_i depth profils the diffusion coefficient of neutral Fe_i could be determined. It was shown to be about one order of magnitude lower than for positively charged Fe_i, as determined from iron acceptor pairing.

A STUDY OF GOLD-TRACER DIFFUSION IN AMORPHOUS SILICON AND ITS SIGNIFICANCE IN REVEALING THE DIFFUSION MECHANISMS OF TRANSITION METALS IN AMORPHOUS SEMICONDUCTORS

W. FRANK and W. GUSTIN
Max-Planck-Institut für Metallforschung, Heisenbergstraße 1
D-7000 Stuttgart 80, Germany

and

S. Coffa, J.M. Poate, and D.C. Jacobson
AT&T Bell Laboratories, 600 Mountain Avenue
Murray Hill, NJ 07947, USA

By means of the target-to-intermediate-target Ar^+ sputtering technique an approximately 150 nm thick layer of amorphous Si—0.66at.%Au was deposited on a glass substrate and, in a subsequent sputtering process, covered by an a-Si layer of about the same thickness. After diffusion annealing and neutron activation the penetration profile of Au in a-Si was determined. This was done by sputtering off the top layer, collecting the material on a foil while this was discontinuously wound up like a film in a camera, and finally measuring the specific radioactivity of the Au on the various foil segments. From such penetration profiles recorded after diffusion annealing at different temperatures, it was found that between 250 and 430° C the diffusion coefficient D of Au in a-Si obeys the Arrhenius law $D = 6.9\times10^{-9}\exp[-(1.5 \pm 0.1)\mathrm{eV}/kT]\ \mathrm{m^2s^{-1}}$.

The results of the precedingly described experiment will be compared to those on the diffusion of transition metals (Cu, Ag, Au, Pt, Pd, Zn) in a-Si obtained by Rutherford backscattering spectroscopy as well as to data on the transition-metal diffusion in c-Si. From this comparison it will be concluded that in a-Si all transition metals so far investigated undergo interstitial-like diffusion that is delayed by temporary trapping, irrespective of whether in c-Si the metals are fast interstitial diffusers (like Cu or Pd) or diffuse via the interstitial—substitutional kick-out mechanism at intermediate rates (like Au or Pt).

Session G

Processing Defects and Defects in Devices

Tuesday, 23 July, 2:00 PM

Perella Auditorium

INTERSTITIAL DEFECT REACTIONS IN REACTIVE ION ETCHED SILICON

J.L.Benton, J.Michel*, L.C.Kimerling*, B.E.Weir, D.J.Eaglesham,
L.C.Feldman, R.A.Gottscho

AT&T Bell Laboratories, Murray Hill, NJ 07974
*MIT, Department of Materials Science and Engineering, Cambridge, MA 02139

Reactive ion etching (RIE) is a key process for pattern transfer in semiconductor device technology. The anisotropic nature of RIE is critical for the realization of silicon submicron design specifications. This work shows that the physical, electrical, and chemical reactions in the near surface region of RIE processed silicon introduce intersititial defects which control the properties of the device material.

Photoluminescence (PL), current-voltage (I-V), transmission electron microscopy (TEM) and Rutherford backscattering (RBS) measurements show that silicon surfaces etched in a CF_4+8%O_2 or SF_6+8%O_2 plasma consists of two distinct regions, a *surface damage region* extending 1000Å from the surface and a *point defect reaction region* which can extend to depths > 1μm. The extent of the *surface damage region* cannot be simply explained by displacement damage mechanisms from the 100-300 eV ion energies alone. We observe that F from the plasma penetrates approximately 1000Å, and that this layer contains a concentration of interstitial defects $\geq 10^{18} cm^{-3}$. The electrical and optical properties of the silicon are both affected by this damaged region.

The depth of the *point defect reaction region* is determined by diffusion limited trapping of the interstitial Si generated during the RIE. It is directly affected by the background impurity concentrations in the substrate silicon. In float-zoned Si, carbon is the dominant impurity, and the formation of C_s–C_i defect pairs are observed with a diffusion length of 5000Å. In Czochralski grown Si, the interstitial defects are trapped by oxygen yielding C_i–O_i pairs with a diffusion length of 500Å. We have determined the reaction kinetics and branching ratios among the defect products and have constructed a model to evaluate the introduction and behavior of the interstitial complexes during processing. We also determined that the long range diffusion of the interstitial carbon is recombination enhanced by the plasma radiation during the dry etch process.

Removal of implantation damage in Cd and In doped InP and GaAs

W. Pfeiffer, M. Deicher, R. Keller, R. Magerle, P. Pross and H. Skudlik
Fakultät für Physik, Universität Konstanz, D-7750 Konstanz, FRG
R. Kalish and N. Moriya
Technion, Haifa 32000, Israel
Th. Wichert and H. Wolf
Technische Physik, Universität des Saarlandes, D-6600 Saarbrücken, FRG
ISOLDE Collaboration
CERN, CH-1211 Geneva, Switzerland

The annealing of implantation damage after heavy ion implantation is crucial for the use of this technique for controlled doping of compound semiconductors. It has been shown that already a very low annealing temperature (300 - 400 K) is sufficient to drive the implanted atoms on substitutional lattice sites [1]. In contrast, an annealing temperature of about 1200 K is necessary to obtain electrical activation of implanted dopants. We used the perturbed angular correlation technique (PAC), a method which is sensitive to the direct structural and electronical environment of the radioactive probe atoms, to investigate the annealing behaviour in the temperature regime between structural recovery and electrical activation. In our investigation we used the radioactive probe atom ^{111m}Cd, which acts as acceptor, and the isoelectronic ^{111}In. In order to connect our results to other investigations and to obtain information on the achieved electrical activation we performed also Hall measurements. The Cd was implanted with 60 keV resulting in a maximal dopant concentration of 10^{18} cm^{-3}. ^{111}In was implanted with 60 keV and 350 keV at comparable doses. The samples were subsequently annealed in a rapid thermal annealing setup.

Our results show that the incorporation of Cd in an unperturbed environment (structural and electronic) occurs at about 900 K in GaAs and 1100 K in InP. This is significantly lower than it is necessary for electrical activation. This difference indicates that the recovery of defects, which are not loccally correlated with the dopant atom, is necessary to achieve electrical activation. ^{111}In and ^{111m}Cd implants exhibit similar annealing behaviour. The incorporation on unperturbed sites in GaAs depends on the total ion dose. Preimplantation with As, Ga and Cd (10^{14} cm^{-2}) shifts the stage to 150 K higher temperature, without influence of the chemical species. We conclude that the reported annealing stage reveals a general annealing mechanism: the removal of intrinsic defects from the more distant environment of the probe atoms.

[1] S. Winter, S. Blässer, H. Hofsäss, S. Jahn, G. Lindner, U. Wahl, and E. Recknagel, Nucl. Instr. Meth. B 48 (1990) 211.

A FLUX ANALYSIS OF POINT DEFECTS DURING SiO_2 PRECIPITATION IN SILICON

William J. TAYLOR, Ulrich M. GÖSELE, Teh Y. TAN
School of Engineering, Duke University
Durham, NC 27706, USA

A conclusion reached from studies of diffusion behavior of dopants and other impurities is that vacancies and self-interstitials coexist in silicon at elevated temperatures. Adopting this conclusion, we investigate the influences of these two types of point defects on SiO_2 precipitate growth over a wide temperature range.

Formation of SiO_2 in silicon involves a volume expansion, creating strain in the surrounding matrix. This strain must be continuously relieved if precipitation is to proceed. For every SiO_2 molecule incorporated into a growing precipitate, we assume strain relief via a point defect: either emission of a self-interstitial (I) or absorption of a vacancy (V). We study the two extreme conditions: volume compensation purely by I or purely by V. In each case, the flux of the point defect must be approximately equal to the flux of oxygen in order to explain the experimentally observed oxygen-diffusion-limited precipitate growth behavior.

For the I-only case, the out-going I flux from a precipitate is determined by the I supersaturation at the interface. During the early stages of precipitation, the generated I remain near the precipitate, forming the supersaturation required for driving the I flux. The growth stage can then proceed as oxygen-diffusion-limited precipitation.

For the V-only case, a continuous incoming flux of V derives from a V undersaturation at the precipitate-matrix interface. The needed V either diffuse in from the surface, or are generated in the bulk via V-I pairs. We have found that these processes are incapable of explaining the observed oxygen-diffusion-limited SiO_2 precipitate growth phenomenon. In-diffusion from the surface provides a V flux too low in magnitude, and I-V pair generation would concurrently induce energetically unfavorable supersaturations of I in the bulk.

We conclude that the strain-relief necessary for SiO_2 precipitate growth to occur can not be accommodated purely via vacancy absorption. However, by allowing self-interstitial emission to contribute to the strain-relief process, the commonly observed precipitate growth behavior can be explained.

DEEP STATES ASSOCIATED WITH COPPER DECORATED OXIDATION INDUCED STACKING FAULTS IN SILICON

M. Kaniewska[a,b], J. Kaniewski[a,b] and A.R. Peaker[b]

a) Institute of Electron Technology, Al.Lotników 32/46, 02-668 Warsaw, Poland, b) Centre for Electronic Materials, University of Manchester, Institute of Science and Technology, P.O. Box 88, Manchester, M60 1QD, England

For manufacturing devices based on Si different technological steps, including oxidation processes, are performed. Then different kinds of extended defects, such as dislocations, stacking faults and oxygen precipitation are generated. It is well known that extended defects, like stacking faults, can increase leakage current in MOS power devices [1]. On the other hand, it is also known that extended defects, especially dislocations, can act as a sink for metals. Additionally, it has been shown that deep states as a result of a common action of metals and stacking faults move to the mid gap [2] and can become detrimental for the device performance.

For the first time in this paper we report the results of investigations of deep levels associated with oxidation induced stacking faults (OSFs) decorated with copper. For this purpose the deep level transient spectroscopy (DLTS) was used. It is found that the emission properties of deep states change according to the specific location of the defect on the OSFs, and their characteristics are strongly modified by the copper diffusion conditions. It is shown that the electrical activity of the extended defect is crucially important when it is decorated with copper. Results of precise DLTS profiling in terms of the gettering effect of metals at the OSFs depending on their size are discussed.

[1] B.O.Kolbesen et al, Inst. Phys. Conf. Ser. 104, 421, 1990
[2] A.R.Peaker et al, Mater. Sci. Eng. B4, 123, 1989

THE PROPERTIES OF INDIVIDUAL Si/SiO_2 DEFECTS AND THEIR LINK TO 1/F NOISE

Michael UREN
Defence Research Agency Electronics Division (RSRE), Great Malvern, Worcestershire WR14 3PS, United Kingdom

The success of the silicon MOSFET is directly attibutable to the near perfection of the silicon/silicon dioxide heterojunction. However typically there remain about $10^{10}cm^{-2}eV^{-1}$ interface defects distributed through the silicon bandgap. This low density means that in a modern submicron MOSFET there is often only one defect with its energy level near the silicon Fermi level and hence able to change its occupancy. This thermally driven change in occupancy leads to a discrete change in the channel conductance which can be easily observed as a two level fluctuation (or random telegraph signal, RTS) in the conductivity.

The ability to observe the independent capture and emission processes from a single defect has allowed the capture kinetics to be investigated in great detail. It is found that both the capture and emission processes are activated and this has been interpreted as strong lattice relaxation occurring on capture. In addition, the defects show a large entropy change on capture, which appears as a temperature dependence of the trap free energy level.

Unlike bulk semiconductor defects, every oxide defect is found to be different having a wide distribution of capture activation energy, cross-section and energy level. The effect of each defect on the channel conductivity is also found to have a different magnitude (sometimes even changing sign). Some RTSs show complex behaviour due to defect-defect interactions and correspondingly complex models are now being developed to explain them. The chemical nature of the defects remains unknown, but I will discuss some of the possibilities.

In the device noise spectrum, each individual defect contributes a noise having a Lorentzian spectrum. I will show how the distribution of defect properties leads in a quite general way to the 1/f spectrum ubiquitously observed in larger MOSFETs. The insensitivity of the final ensemble noise spectrum to the details of the defect property distributions makes it a poor tool for the study of the defects responsible. Indeed it appears that progress can only be made in this field through a knowledge of the individual defect characteristics.

Hydrogen Induced Defects and Defect Passivation in Silicon Solar Cells

Bhushan L. Sopori
Solar Energy Research Institute
1617 Cole Boulevard
Golden, Colorado 80401

It is well established that hydrogen can passivate crystal defects to improve the performance of silicon solar cells. However, commercial use of hydrogenation for impurity/defect passivation has been limited by somewhat complex behavior of hydrogen in silicon. For example, it has been observed that hydrogen passivation can improve only the low-performance cells and that long process times are needed to diffuse hydrogen deep within the bulk of the substrate. In order to understand these issues it is necessary to develop a coherent model of synergistic effects of hydrogen interactions including dopant deactivation, recombination due to hydrogen induced defects as well as defect/impurity passivation. In this paper we will discuss the results of our studies on hydrogen-induced defects and the interaction of hydrogen with grown-in defects when hydrogen is introduced by low-energy implantation. We also discuss a back-side hydrogenation technique which can circumvent these problems and take advantage of the hydrogen induced defects.

Three different types of defects are observed due to such a process:

1. Near-surface damage in the form of dislocation loops, stacking faults, and punched-in dislocations. The depth of damage increases with the ion energy and the hydrogen concentration at the surface.
2. Formation of platelets which reside in (111) habit planes and appear to be related to the vacancy collapse mechanism. This evidence comes from XTEM/HRTEM studies and investigations into the relationship of such platelets on the non-equilibrium defects.
3. Decoration of the grown-in dislocations by hydrogen, seen as "hydrogen bubbles". It is determined that in some cases such bubbles can also act as sources of new dislocations.

It is determined that most of the hydrogen in the bulk of the substrate stays optically and electrically inactive. However, the defects introduced by hydrogenation can have deleterious effects on the solar cell performance, especially when hydrogen is introduced from the front (junction) side of the cell. Likewise, deactivation of boron near the junction can also affect cell performance. In order to minimize these effects it is necessary to introduce hydrogen from the backside of a solar cell. We will describe a back-side hydrogenation technique for solar cells and describe passivation characteristics of solar cells fabricated on commercial substrates grown by different techniques. We propose that, due to high carrier recombination at hydrogen-induced defects, it is likely that the degradation effect can overcompensate the primary passivation. This process can limit the effectiveness of hydrogen passivation.

DEFECTS AND SCHOTTKY BARRIER FORMATION: A POSITIVE PROOF FOR EPITAXIAL Al ON AlGaAs SCHOTTKY DIODES

J. M. Langer[a,b] and P. Revva[b]
[a]Institute of Physics, Polish Academy of Sciences, Warsaw, Al. Lotnikow 32/46, Warsaw, Poland and [b]The University of Manchester Institute of Science Technology, Sackville Str., P.O.Box 88, Manchester M60 1QD, England

The origin of the Fermi level pinning in metal-semiconductor (MS) junctions has been vigorously debated for a long time. Several models predict that it is the same screening at the interface which causes the Fermi level pinning in Schottky barriers and aligns bands in semiconductor heterojunctions. It has been argued, however, that the Fermi level pinning is caused by the interface defects generated during the metal deposition. Most of arguments of the proponents of the first concept rely on the positive energy correlation of the Schottky barrier heights and computed neutrality levels of the semiconductors. The concept of the Fermi level pining via defects lacks definite verification due to unability to detect those defects that cause the pinning.

In order to test validity of either of the two models we have measured temperature dependence of the Schottky barrier height of the MBE grown epitaxial Al on p- and n-type AlGaAs MS junctions. The temperature shifts of the conduction and valence bands can be approximated as a sum of two components. One is a simple lattice dilation (hydrostatic component) and the second is related to the temperature dependence of the electron phonon coupling (Debye-Waller factor). All theories predict that in GaAs the dominant shift occurs in the valence band. In the indirect gap AlGaAs *almost all* temperature dependence of the energy gap comes from the temperature shift of the valence band because of the cancellation of dilation and Debye-Waller components. If the neutrality concept of the Fermi-level pinning would be valid, the temperature dependence of the Schottky barrier on a p-type AlGaAs should be comparable with such a dependence on an n-type direct gap AlGaAs. In the indirect gap AlGaAs the temperature dependence of the Schottky barrier height should be close to that of the energy gap for the p-type material and very weak for the n-type substrate.

In all structures measured temperature dependence of the Al/AlGaAs(n-type) equals within the experimental error to the temperature dependence of the energy gap (for all AlGaAs compositions, i.e. from GaAs to AlAs). The temperature dependence of the barrier height on the p-type material is much weaker, if any. This result is in direct conflict with the neutrality level concept, but has obvious explanation if the interface defects whose ground state is of the bonding type are responsible for the pinning. Ionization of such defects leads to a local bond-breaking and the change of the phonon frequencies. Therefore, the ionization entropy of such defects must be large. Because of the similarity to the bond breaking in the valence to the conduction band transitions, ionization entropy of such defects should be close to that of the semiconductor energy gap [1]. We conclude therefore, that the Fermi level pinning in the high quality epitaxial Al/AlGaAs MS junctions is indeed due to the interface defects. We believe that the reported result is the first positive proof of a dominant role of defects in the formation of the Schottky barrier height.

[1] Van Vechten J. and Thurmond C. D. Phys. Rev. B 14, 3539 (1976).

Recombination-enhanced diffusion of Be in GaAs

Masashi UEMATSU and Kazumi WADA
NTT LSI Laboratories,
3-1, Morinosato Wakamiya, Atsugi-shi, 243-01, JAPAN

Device degradation under operation is a widely observed phenomenon in such devices as Be-doped AlGaAs/GaAs HBTs, Esaki diodes, light emitting diodes and laser diodes. In these cases, degradation tends to occur during forward bias operation, indicating that minority carrier injection, i.e., recombination processes, plays an essential role in the degradation.

The present paper describes recombination-enhanced diffusion of Be in GaAs by investigating current-induced degradation of Esaki diodes. The enhanced Be diffusion coefficients D_{Be} and their decreases with time are obtained. The possible mechanism for the enhanced diffusion is discussed based on the analysis in terms of the kinetics of the decay of the recombination center.

The tunnel diodes were fabricated by MBE, using Be (4×10^{19} cm^{-3}) as a p-type dopant and Si (1×10^{19} cm^{-3}) as an n-type dopant. The well-known degradation of Esaki diodes, i.e., decreases in peak current densities (J_p), was reproduced under forward bias operation. The degradation by thermal annealing was also investigated under a zero-biased condition. Based on Buckingham's formula (1963), D_{Be} and its decrease are obtained by the rates of decreasing J_p.

The Be diffusion under forward bias is enhanced by a factor of about 10^{15} at room temperature, and the difference in the activation energies between the current-induced and the thermal diffusion is about 1.2 eV (Fig. 1). These results suggest that the energy of 1.2 eV released on minority carrier injection enhances the Be diffusion.

Analyzing the time dependence of the D_{Be}, the rates of decreasing J_p were found to decline with elapsed time, an indication of decreasing D_{Be}. These decreases are well described by a single exponential decay up to about 30 % decay of J_p (Fig. 2). To account for these decreases, the following model is proposed. Recombination-enhanced annealing (Lang & Kimerling, 1974) of the recombination centers occurs concurrently with the degradation, and this decay is the rate-determining step of the process. When the recombination center is annihilated, a certain point defect is emitted, which governs the Be diffusion. Following Tan & Gösele, the Be diffusion is governed by the supersaturation of interstitial Ga atoms (I_{Ga}). Decreasing J_p with time was simulated based on the model, and the results matched the observed curves very closely.

The temperature and time dependences of the D_{Be} lead us to conclude that the recombination event enhances the Be diffusion, which we name <u>recombination-enhanced impurity diffusion (REID)</u>. The present study may indicate a novel approach in which the generation kinetics of point defects by recombination-enhanced processes can be elucidated in terms of dopant diffusivity enhancement.

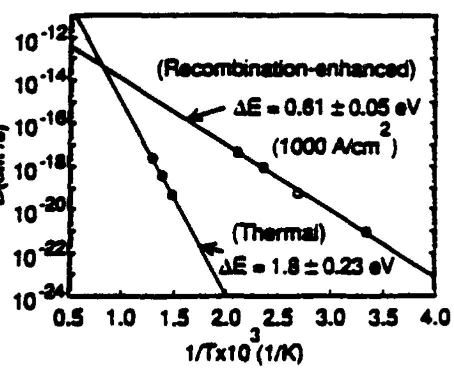


Fig. 1 Recombination-enhanced and thermal diffusion coefficients of Be.

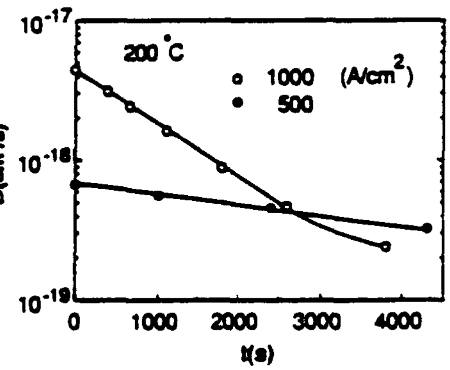


Fig. 2 Decrease in Be REID coefficients

Session H

Donors in Compound Semiconductors - I

Wednesday, 24 July, 8:30 AM

Physics Auditorium

Defect metastability in III-V compounds

Matthias Scheffler[(*)]

Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4-6, D-1000 Berlin-33, Germany

We discuss parameter-free density-functional-theory calculations of various defects in III-V compounds. We concentrate on anion-substitutional single and double donors, but also mention some results for cation-site centers. The defect-induced electronic structure and wave functions are analysed, and it is shown that a defect metastability between the tetrahedral substitutional site and the vacancy-interstitial pair is a general property of III-V compounds. The conditions under which this metastability may be observable by experiments are found to depend sensitively on local pressure (e.g. due to alloying), external pressure, and the defect charge state.

We also present an overview of the properties of $EL2$ and DX centers in GaAs, and discuss their similarities as well as their differences. The above mentioned type of metastability is identified to lead to the exciting properties of these two centers (e.g. a shallow-deep transition and a negative U behavior for DX). Alternative theories are discussed as well, and open questions (i.e. not yet explained experimental data) are addressed.

[(*)] in collaboration with Jarosław Dąbrowski

HIGH PRESSURE STUDIES OF ELECTRONIC STATES WITH SMALL LATTICE RELAXATION OF DX CENTRES IN GaAs

J.E. DMOCHOWSKI[1,2], P.D.WANG[1], and R.A. STRADLING[1]

[1]*IMPERIAL COLLEGE OF SCIENCE, TECHNOLOGY AND MEDICINE*
Prince Consort Road, London SW7 2BZ, UK

[2]*INSTITUTE OF PHYSICS, POLISH ACADEMY OF SCIENCES,*
Al. Lotnikow 32/46, 02-668 Warszawa, POLAND.

The origin of DX-centre is still controversial. A weakly relaxed A_1 antibonding state of substitutional impurity and strongly relaxed, broken-bond interstitial impurity-vacancy complex are two mostly advocated candidates for DX-like states of donor impurities.

We present here experimental investigations in which we demonstrate that both A_1 antibonding states and DX-like states should coexist. We investigate different donor species: Sn, S, Si and Ge in high purity GaAs at high hydrostatic pressures.

Using developed on purpose diamond anvil cell technique for far-infrared transmission experiments we monitor shallow donor absorption as a function of high hydrostatic pressure. We demonstrate that shallow donor absorption is quenched by species-specific electronic states of impurities which enter the gap for pressures lower than expected for X-like effective mass states. Unlike DX-like states in $Al_xGa_{1-x}As$ these states quench shallow donors persistently i.e. these deep states cannot be metastably photoionized. At pressures above this shallow-deep transition deep states can be observed in luminescence and have pressure coefficient different from both Γ and X minimum.

Very weak anticrossing effects between the deep state and shallow $1s(A_1)(\Gamma)$ states are characteristic for group IV Ge, Sn and Si donors. The Γ-X mixing is, however, most likely reason for stronger deviation from hydrogenic behaviour observed for sulphur Γ-shallow donor. The A_1 symmetry and larger ionization energy expected for the ground states of group VI X-bound effective mass donors, both can considerably enhance the Γ-X shallow states interaction.

The presented above results give evidence for weakly relaxed non-metastable deep states which have all atributes of A_1 antibonding states of substitutional impurities. These states must coexist with DX-like states to explain metastability effects observed in other experiments e.g. transport, DLTS.

Vibrational Mode Fourier Transform Spectroscopy with a Diamond Anvil Cell: Modes of the Si DX Center and S-related Complexes in GaAs*

J. A. Wolk and E. E. Haller
Lawrence Berkeley Laboratory and University of California at Berkeley

M. B. Kruger, R. Jeanloz, and J. N. Heyman
University of California at Berkeley

W. W. Walukiewicz
Lawrence Berkeley Laboratory, Berkeley, Ca. 94720, USA

Using Fourier transform absorption spectroscopy with a diamond anvil cell, we have observed a local vibrational mode (LVM) of the DX center in heavily doped GaAs:Si. We have also found a previously unobserved set of three local vibrational mode peaks in highly doped GaAs:S. Absorption spectroscopy on heavily doped, unirradiated n-type GaAs can only be performed at high pressures where DX centers form, trapping all free carriers. The need for large pressures combined with optical access requires that these observations be made with the samples mounted in a diamond anvil cell, and these results represent the first time semiconductor defects have been studied by this technique.

We have observed a new LVM peak in highly doped GaAs:Si which can only be observed under hydrostatic pressure greater than 23 kbar. This new mode is distinct from the well known Si_{Ga} substitutional shallow donor LVM peak, which is the only other LVM peak observed in our samples. We identify this new peak as an LVM of the Si DX center. We have observed how both LVM frequencies shift with pressure, and find that these shifts are linear over the pressure range of our observations (0 - 40 kbar). They are given by $d\nu_{Si_{Ga}}/dp = 0.66 \pm 0.03$ cm^{-1}/kbar and $d\nu_{Si_{DX}}/dp = 0.61 \pm 0.04$ cm^{-1}/kbar. By combining resistivity and Hall effect data with the ratio of the area in the LVM absorption peaks for the two defects we conclude that the DX center is negatively charged.

The frequencies of the three new local vibrational modes seen in heavily doped GaAs:S have been observed as a function of pressure. Extrapolations of these pressure dependences imply that the zero pressure frequencies for these modes should be 312 cm^{-1}, 317 cm^{-1}, and 321 cm^{-1}. Since these modes have been observed in crystals that were cooled very slowly during growth but not in crystals grown by the Czochralski method, we propose that they are due to S-related complexes. SIMS results on these samples show that S is the only impurity present in concentrations large enough to be observed with our technique. Work is in progress to positively identify the centers responsible for these new LVMs.

Various types of optical spectroscopy have been performed on defects in semiconductor samples mounted in diamond anvil cells. For example, photoluminesence[1] has been done for many years and magneto-spectroscopy transmission experiments[2] have also recently been reported. These techniques use a laser as a light source. In order to do Fourier transform spectroscopy, however, a blackbody broadband light source, which is far less intense than a laser, must be used. For this reason, Fourier transform spectroscopy has only been successfully used to observe intrinsic defects ($n = 10^{22}$ cm^{-3}). We have extended this technique to the study of impurities by constructing a monolithic assembly which has a light concentrating cone in front of the diamond anvil cell and a Ge:Be photoconductor detector designed to operate at low photon fluxes mounted directly behind the cell.

1) M. Gerling, X. Liu, S. Nilsson, M. E. Pistol, and L. Samuelson, Semicond. Sci. Tech., 4, 257 (1989).
2) J. E. Dmochowski, P. D. Wang, and R. A. Stradling, Semicond. Sci. Tech., 6, 118 (1991).

* Work supported by US DOE under Contract DE-AC03-76SF00098 and US NSF under Grants DMR-88-06756 and EAR-89-03801

Optically-Detected Magnetic Resonance Studies of Donor States in $Al_xGa_{1-x}As$ ($x \geq 0.35$) Doped with Group-IV and Group-VI Impurities

E.R. Glaser and T.A. Kennedy
Naval Research Laboratory, Washington, D.C. 20375-5000

It is important to understand the nature of both the deep and shallow levels that arise from the doping of GaAs and AlGaAs crystals with either group-IV or group-VI impurities. There has been a concerted effort recently to obtain information on these donor states, such as the charge state and symmetry behavior, from magnetic resonance studies. Electron paramagnetic resonance (EPR) and optically-detected magnetic resonance (ODMR) experiments have been successful in clarifying the nature of the shallow states associated with the X-point conduction band (CB) minima in n-doped $Al_xGa_{1-x}As$ with $x \geq 0.35$. In this work, the results of extensive ODMR experiments performed by our group on n-doped epitaxial layers of AlAs and $Al_xGa_{1-x}As$ ($x \geq 0.35$) grown on (001) GaAs substrates are reviewed. The AlGaAs layers were doped during growth or via implantation with Si and Sn from group-IV and S, Se, and Te from group-VI. Symmetry information was obtained from angular rotation studies with the magnetic field rotated in the (110) and (001) planes. Also, uniaxial stress along the [110] and [100] directions has been combined with ODMR to further probe the symmetry of the donor wavefunction.

The donor state in Si-doped AlAs can be described by the usual hydrogenic effective-mass (HEM) theory for substitutional donors on the group-III site associated with the X-point CB minima. The g-value anisotropy and splitting observed from the rotation studies in the (110) and (001) planes, respectively, can be understood using an independent valley model.[1]

The results obtained for the AlGaAs layers doped with S, Se, and Te can be described by the HEM theory modified by a finite valley-orbit (i.e. central cell) interaction that mixes the states derived from the X_x, X_y, and X_z valleys to form an A_1 ground state as predicted by Morgan.[2] Analyses of these results within the virtual crystal approximation yield valley-orbit splitting energies (i.e. chemical shifts) of ~ 16-20 meV for these group-VI donors in $Al_{0.6}As_{0.4}As$.

The nature of the donor states in the Si-doped $Al_xGa_{1-x}As$ heterostructures with $x < 1$ is more complicated. The monotonic decrease in both the g-value anisotropy and splitting and the increase in the linewidth of the donor resonances with decreasing Al mole fraction are attributed to the breakdown of the independent valley model employed to describe the symmetry of the donor ground state in Si-doped AlAs. Various mechanisms that can potentially influence the properties of the donor ground state in Si-doped $Al_xGa_{1-x}As$ with $x < 1$, such as a finite spin-valley interaction, L-X (or Γ-X) interband and X_x-X_y intervalley mixing, and alloy disorder, are discussed. Uniaxial stress experiments provide evidence that the symmetry of the donor wavefunction at x=0.4 is still X-like.

The results for the Sn-doped AlAs and $Al_xGa_{1-x}As$ heterostructures grown by OMVPE indicate that the optically-active states are much deeper compared to the Si donor states. These results contrast with a recent magnetic resonance observation of a shallow donor level derived from the X-point in a Sn-doped $Al_{0.68}Ga_{0.32}As$ sample grown by LPE.[3]

R.S. Sillmon, M.G. Spencer, M. Mizuta, and T.F. Kuech are gratefully acknowledged for providing the samples investigated in these studies. Work supported in part by the Office of Naval Research.

1. E. Glaser *et al.*, Phys. Rev. B40, 3447 (1989).
2. T.N. Morgan, Phys. Rev. Lett. 21, 819 (1968).
3. W. Wilkening *et al.*, to appear in Semicond. Sci. Technol., 1991.

COEXISTENCE OF DEEP AND SHALLOW PARAMAGNETIC EXCITED STATES OF THE DX CENTER IN GaAlAs.

H.J. von Bardeleben, M. Sheinkmann*, C. Delerue** and M. Lannoo**
Groupe de Physique des Solides de l'Université Paris 7,
Centre National de la Recherche Scientifique,
Tour 23, 2 Place Jussieu, 75251 Paris Cedex 05, France

*Institute of Semiconductors, Ukrainian Academy of Sciences,
Prospect Nauki, 45, 252650 Kiev 28, USSR

**I.S.E.N., Laboratoire de Physique des Solides,
41, boulevard Vauban, 59061 Lille Cedex, France

The magnetic resonance techniques are well adapted to study the strongly disputed issue of the electronic and atomic configuration of group IV and group VI donors in GaAlAs alloys (1). Unfortunately, in none of these studies a paramagnetic state of the DX ground state could be observed and the paramagnetic donor states studied after photo-excitation were interpreted by shallow effective mass states (2,3) which are rather insensitive to any local distortion. Very recently it has been shown in the case of the Sn donor that besides the effective mass state a deep donor state, characterized by a high electron localization of ~ 20 % on the central donor atom giving rise to a resolved central hyperfine interaction, can be observed in a limited alloy composition range (4-6). We present new experimental electron paramagnetic resonance and photo Hall results and theoretical modelizations for the alloy dependence of the properties of the deep donor state, which we attribute to the one-electron A_1 antibonding state. The hyperfine interaction is confirmed by the use of isotopically enriched (^{119}Sn) samples. The variation of the g-factor and hyperfine interaction of the deep donor state with the alloy composition are discussed in the framework of mixing of the A_1^{ab} state with A_1 effective mass states. To address the charge state of the apparently diamagnetic DX ground state quantitative, correlated photo EPR and photo Hall measurements have been performed on the same samples. The thermally activated decline of both the paramagnetic donor state as well as the photo carrier has been analyzed in $U < 0$ and $U > 0$ models. The results are compared to those obtained by us for the group VI donor Te. The coexistence range of the deep paramagnetic A_1^{ab} state with the shallow effective mass states $A_1(\Gamma)$, $T_2(X)$, $A_1(X)$ is analyzed within the expected alloy variation of the A_1^{ab} state taking into account the chemical shift of the various donors.

REFERENCES

1. The physics of DX centers in GaAs alloys. Ed. J.C. Bourgoin, Sol. State Phenomena 10, Sci. Tech Publ. (1990).
2. T. Kennedy, in ref. 1.
3. H.J. von Bardeleben, in ref. 1.
4. M. Fockele and J.M. Spaeth, Mat. Science Forum 65, 443 (1990).
5. H.J. von Bardeleben, J.C. Bourgoin, C. Delerue and M. Lannoo, unpublished.
6. H.J. von Bardeleben, Semicond. Sci. and Technol., to be published (1991).

MAGNETIC RESONANCE OF X - POINT SHALLOW DONORS IN AlSb:Te BULK CRYSTALS AND UNDOPED AlSb MBE LAYERS

W. Wilkening, U. Kaufmann, J.Schneider and E.Schönherr*

Fraunhofer-Institut für Angewandte Festkörperphysik,
Tullastrasse 72, D - 7800 Freiburg, Fed. Rep. Germany

*Max-Planck-Institut für Festkörperforschung,
Heisenbergstrasse 1, D - 7000 Stuttgart, Fed. Rep. Germany

F R. Glaser, B.V. Shanabrook, J.B. Waterman and R.J. Wagner

Naval Research Laboratory, Washington, DC 20375-500, USA

We report electron-paramagnetic-resonance (EPR) results for two bulk n-type AlSb:Te crystals with carrier concentrations of $7x10^{16}$ cm^{-3} and (5-8) x 10^{17} cm^{-3} as well as optically detected magnetic resonance (ODMR) data for undoped molecular-beam-epitaxy grown AlSb layers on (001) semiinsulating GaAs substrate.

The bulk materials reveal an isotropic EPR signal at $g = 1.878 \pm 0.005$. In both samples its peak-to-peak amplitude is enhanced by a factor of 30 following illumination with a tungsten/quartz light source. For three reasons we assign this new resonance to the 1s (A_1) ground state of the shallow Te donor associated with the X-point conduction band minima in the indirect gap material AlSb: First, the bulk crystals are Te doped. Second, the significant shift of the g-factor from the free electron value is close to that expected from Roth's formulas. Third, the g-shift is close to the value obtained by scaling the experimental g-shift of group VI donors in AlAs with the ratio of the valence band spin-orbit splittings of AlSb and AlAs. The fact that the optical enhancement factor of the donor EPR amplitude is the same in both samples suggests a DX-type bistable donor behavior rather than neutralization of compensated donor - acceptor pairs.

Photo-luminescence measurements on the AlSb MBE layer revealed a broad featureless emisson band peaked at 0.95 eV. An isotropic ODMR line was observed on this band. Its g-value, $g = 1.883 \pm 0.005$, within the error limits, is identical with that found from the present EPR on bulk Te doped AlSb. Therefore the ODMR line in the nominally undoped MBE layers is attributed to Te and/or some other group VI impurity such as S or Se. This suggests that the emission band observed arises from recombination between a shallow donor impurity and a deep level defect.

The work done at NRL was supported in part by Office of Naval Research.

PHOTOCONDUCTIVITY SATURATION OF AlGaAs:Si EVIDENCE FOR NEGATIVE U

W. Jantsch[a], Z. Wilamowski[b], and G. Ostermayer[a]

[a]Institut für Experimentalphysik, Johannes-Kepler-Universität, A-4040 Linz - Auhof, AUSTRIA

and:

[b]Institute of Physics of the Polish Academy of Sciences, Al. Lotnikov 32/46, 02-668 Warsaw, POLAND

We report investigations of the steady state photoconductivity of heavily doped $Al_xGa_{1-x}As$:Si, which provide a new type of criterion for negative U. This c iterion is based on the investigation of the capture process and its dependence on the free electron quasi-Fermi level E_F^*.

Under illumination, DX centers are ionized at some temperature independent rate. The steady state carrier concentration and thus E_F^* are governed by recapture to the deep DX state. At high temperatures, the capture barrier is transparent and E_F^* is pinned to the donor level $E_{D^{0/+}}$ for $U > 0$ and to $\frac{1}{2}\cdot(E_{D^{0/+}} + E_{D^{-/0}})$ for $U < 0$. At low temperatures, however, we expect a linear increase of E_F^* from detailed balance equations. For $U > 0$, E_F^* approaches the barrier energy E_B for $T \to 0$, whereas for $U < 0$ it extrapolates towards $E_B/2$. For $U > 0$, we therefore expect a difference of E_F^* between the high- and the low temperature limits of $(E_B-E_{D^{0/+}})$, which is equal to the emission barrier. For $U < 0$, in contrast, this difference is $\frac{1}{2}\cdot[E_B- (E_{D^{0/+}} + E_{D^{-/0}})]$. which is just half of the emission barrier if we assume a purely vibronic nature of the latter and hence a two-electron emission process.

The variation of E_F^* can be determined experimentally from the temperature dependent carrier concentration in Hall effect investigations under illumination. For $Al_xGa_{1-x}As$ with $x = 0.31$ and $N_{Si} = 2\cdot10^{18}cm^{-3}$ we observe a linear variation of E_F^* between 50K and 150K. For higher T, E_F^* saturates because of pinning to the donor state as expected. For $T < 50K$, E_F^* also saturates possibly because of pinning to the unrelaxed $E_{D^{0/+}}$ level. Extrapolating the linear part for $T \to 0$ we obtain a variation of E_F^* of 0.2eV. Literature values for the emission barrier are close to 0.4eV which proves the existence of a two-electron, negative U ground state of the Si-DX center in AlGaAs. It also excludes the participation of an intermediate one-electron state in the thermal emission process. The experimental data for E_F^* are explained quantitatively by model calculations which include alloy splitting and level broadening of the DX centers due to Coulomb potential fluctuations.

Session I

Wide Band-Gap Materials

Wednesday, 24 July, 8:30 AM

Perella Auditorium

PHOTOLUMINESCENCE EXCITATION SPECTROSCOPY OF CUBIC SiC GROWN BY CHEMICAL VAPOR DEPOSITION ON Si SUBSTRATES

J.A. FREITAS, Jr.
Sachs-Freeman Associates, Landover, MD 20785, USA

P.B. KLEIN
Naval Research Laboratory, Washington, DC 20375, USA

and S.G. BISHOP
Center for Compound Semiconductor Microelectronics, University of Illinois, Urbana, IL 61801, USA

Photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopy have been applied to the characterization of thin films of undoped and aluminum-doped cubic (3C) SiC grown on Si substrates by chemical vapor deposition. Specific observations[1] include PL spectra attributable to excitons bound to 54 meV neutral nitrogen donors, free-to-bound PL transitions involving aluminum acceptors, nitrogen-aluminum donor-acceptor pair (DAP) recombination (N-Al DAP bands), and a deep DAP band which reveals an unidentified 470 meV acceptor.

Low temperature (6K) PLE spectra have now been obtained using a double grating monochromator and a xenon lamp as a tunable source of excitation. For undoped, n-type films of cubic SiC, plots of the integrated PL intensity, in the range 2.2-1.5 eV, as a function of the wavelength of the exciting light are in excellent agreement with optical absorption spectra reported by Choyke et al.[2] for bulk 3C-SiC. The observed shape of the absorption edge is characteristic of phonon assisted indirect transitions, and spectral features attributable to LA and TA phonons are discernible. No below-gap, extrinsic absorption features are observed in the PLE spectra of the undoped films. These results demonstrate the use of the PLE technique for bandedge absorption measurements in thin semiconductor films for which transmission measurements are not practical.

The intense N-Al DAP PL bands (2.2-1.5 eV) observed in Al-doped films provide much improved signal-to-noise ratios for the PLE spectra in these samples compared to those obtained in the undoped films. In addition to the characteristic above-gap indirect absorption edge spectrum, the PLE spectra for the Al-doped samples exhibit below-gap, extrinsic absorption features at photon energies corresponding to the nitrogen bound exciton peaks observed in the PL spectra. These extrinsic, nitrogen donor-related features in the PLE spectra are observed only in the Al-doped films in which the nitrogen donors have been compensated by the aluminum acceptors The extrinsic absorption process which contributes to the excitation of the N-Al DAP PL is apparently a photoneutralization of the compensated (positively charged) nitrogen donors.

1. S.G. Bishop and J.A. Freitas, Jr., J. Cryst. Growth 106, 38(1990).
2. W.J. Choyke, D.R. Hamilton, and L. Patrick, Phys. Rev., 133,A1163(1964).

Paramagnetic defects in SiC based materials

O. CHAUVET, L. ZUPPIROLI, I. SOLOMON[a]
Y.C. WANG[b], R.F. DAVIS[b]

E.P.F.L., Lab. Phys. Sol. semi-cristallins, I.G.A.-D.P., Ph B, ECUBLENS, CH-1015 LAUSANNE, SWITZERLAND
PHONE: (41) 21-693-33-96
FAX: (41) 21-693-44-44

Point defects and impurities play a major role on the electronic properties of silicon carbides. Electron Spin Resonance (ESR) was used to investigate the magnetic properties of both native and irradiation induced defects. Our experiments covered a wide variety of materials: glow discharge a-$Si_{1-x}C_x$:H with low carbon content (x<15%), electron irradiated ß-SiC single crystals, nanocrystalline SiC fibers and SiC industrial powders. We were able to identify the the silicon vacancy or the carbon antisite (thanks to a hyperfine spectrum), the carbon vacancy (thanks to the silicon dangling bonds spectrum) and carbon complexes with sp^2 hybridization. A common point in all the materials studied (except the single crystals before irradiation) is the presence of sp^2 carbon, even in low carbon content amorphous SiC (x~15%). Oxygen impurities play a peculiar role at low temperatures. Evidence is given that the silicon dangling bonds have an almost zero or negative effective Hubbard energy. Nanostructural effects dominate the ESR properties of SiC fibers.

(a) *Ecole Polytechnique, Lab. P.M.C., 91128 PALAISEAU cedex, FRANCE*
(b) *North Carolina State University, Dpt. Mat. Sci. and Eng., BOX 7907, RALEIGH NC 27695-7907, U.S.A.*

Transition Metals in Silicon Carbide

J. Schneider

Fraunhofer-Institut für Angewandte Festkörperphysik
Tullastraße 72, 7800 Freiburg Germany

Silicon carbide (SiC) finds currently renewed interest as an electronic material for devices operating under extreme conditions, which are not met by silicon. A survey is given of recent progress made in identifiying and understanding deep level defects in SiC. Emphasis will be on transition metals, in particular on the 3d-elements vanadium and titanium, which are now known to be omnipresent trace impurities in Lely-grown SiC-polytype crystals.

Vanadium, substituting for silicon in SiC, has been identified as an amphoteric deep level defect. Electron Spin Resonance (ESR) is observed for the neutral state $V^{4+}(3d^1)$, $S = 1/2$, and for the A^--state $V^{3+}(3d^2)$, $S = 1$. By photo-ESR, the position of the (0/+) donor level is found to occur near midgap in 6H-SiC. Near-infrared, 1.3 - 1.5μm, photoluminescence and absorption, arising from internal 3d-shell transitions, $^2T_2 \rightarrow {}^2E$, are observed for the neutral state $V^{4+}(3d^1)$. These sharp-line spectra were found to be very specific for a given SiC-polytype.

Isoelectronic, electrically inactive, titanium impurities have been found, by ESR, to complex preferentially with shallow nitrogen donors. The resulting Ti_{Si}-N_C pair then acts as deep donor, E_C - 0.6 eV, in 6H-SiC. Also presented are novel ESR-data for the shallow nitrogen donors in 4H- and 6H-SiC, revising previous views about the localisation of the donors' wavefunction.

Impurity-defect reactions in ion-implanted diamond

Alexey A. GIPPIUS

P.N.Lebedev Physical Institute of the Academy of Sciences of the USSR, Leninsky prospect 53, Moscow 117924, USSR

1.Introduction. The major factor determining the type and parameters of impurity-defect reactions in ion-implanted solids is high local and (at higher fluences) high average density of radiation defects. An additional factor essentual in natural diamonds is high concentration of background impurities of which the most important is nitrogen known to exit in several aggregate forms. The paper to be presented deals with luminescent control of reactions involving implanted impurities, radiation defects and background impurities in ion-implanted and annealed natural diamonds.

2.Luminescent control of defects and impurities in solids is based upon the accumulated data on the nature and properties of the appropriate centres. The first part of the paper is meant to summarise these data with the emphasis on new centres recently observed by the author and related to oxygen, transition elements (Ni, Ti, Nb) and various aggregate form of nitrogen . It is noted that luminescent spectral analysis should take into account both the intensities of lines (related to concentration of centres) and their widths (related to lattice disorder and impurity-defect interaction).

3.Impurity-defect reactions within disordered regions produced by displacement cascades are governed by very high local density of defects. In this case the reactions between intrinsic defects dominate while the formation of defect-impurity complexes saturates. These effects tend to increase with the increase of ion mass. Relatively heavy ions (such as Ni) were found to reside within the regions whose structure should be understood not in terms of point defects but rather in terms of gross lattice disorder related to ion tracks which survive the highest annealing temperatures close to the limit of stability of diamond. The effects of interaction between the tracks and of their overlapping are described.

Reactions of association of single nitrogen atoms into aggregates (implying the mobility of the impurities) are observed in ion implanted samples at considerably (500-1000°C) lower temperatures than in samples not irradiated or irradiated by fast electrons. This irradiation enhancement of the reactions is due to high average density of defects produced either by mobile components of the displacement cascades or by overlapping of disorder regions. Large nitrogen aggregates such as the so called B-form were found to decompose at these conditions producing a number of impurity- defect complexes.

Kind of gettering effect was observed in samples implanted with titanium or oxygen where a number of lines were quenched possibly due to decrease of availability of defects needed for the formation of corresponding defect-impurity complexes. The release of implanted (and trapped) oxygen from optically inactive defect-impurity aggregates was observed after subsequent irradiation and annealing.

Hydrogen release from internal sources where it is "stored" in optically (and electrically) inactive form was observed. In natural diamond these sources are believed to be magma droplets.The process is important in view of hydrogen passivation of impurities recently observed also in diamond.

ODMR INVESTIGATIONS OF THE A - CENTRES IN CdTe

D. M. Hofmann, P. Omling, H. G. Grimmeiss, B. K. Meyer, D. Sinerius** and K.W. Benz***

Solid State Department, University of Lund, Sweden

*Physikdepartment E16, Technical University of Munich, James Franck Str., 8046 Garching, F.R.G.

**University of Freiburg, Kristallographisches Institut, Hebelstr. 25, 7800 Freiburg, F.R.G.

The single acceptor, a Cadmium vacancy paired with a nearest neighbour donor impurity (A - center), plays an important role in the self compensation mechanism in II - VI compounds.
To determine the structure of the A - centres in CdTe optically detected magnetic resonance (ODMR) investigations have been performed on Cl doped crystals grown by the vertical Bridgeman technique.
The ODMR signals have been detected as microwave induced changes of the magnetic circular polarisation of the emission (MCPE) of the A - center luminescence band located around 1.42 eV (1.6 K). Donor as well as acceptor resonance signals have been observed. The Cl - donor resonance is isotropic with g = 1.69. The acceptor resonances are strongly anisotropic. The analysis of the ODMR angular dependence reveals that the defect has trigonal symmetry (C_{3v}). The g - factors are $g_{\parallel} = 2.2$ and $g_{\perp} = 0.4$, assuming an effective spin S = 1/2. These g - factors are interpreted by considering the effect of the crystal field on a J = 3/2 (Γ_8) hole bound to the vacancy - donor pair defect.
In addition the interactions of the nearest Tellurium neighbours could be resolved and have been analysed.
These properties of the A - centres in CdTe differ remarkably from the well known V_{Zn} - donor impurity complexes in ZnS and ZnSe where the defects show deep level properties with g - factors close to two.

PICOSECOND ENERGY TRANSFER BETWEEN EXCITONS AND DEFECTS IN II-VI SEMICONDUCTORS

I.Broser, A.Hoffmann, C.Fricke and R.Heitz

Institut für Festkörperphysik
Technische Universität Berlin, Germany

The dynamical behaviour of intrinsic excitations in semiconductors is strongly influenced by defects, which serve as efficient traps. The purpose of this paper is to study the relevant relaxation and energy transfer processes by time resolved investigations of free and bound excitons in II-VI semiconductors using time correlated single photon counting and pump-and-probe technics. The dynamical behaviour of the exciton luminescences has been investigated for differently doped crystals.

The decay of the bound exciton luminescences in CdS, ZnO, ZnS and ZnSe has been studied, showing in all four host materials an increase of bound exciton lifetimes with increasing binding energies. Either the hole or the electron from the exciton will become stronger localized leading to a poorer overlap of both wavefunctions and therefore to a lower oscillator strength. Lifetimes between 30ps and 1085ps have been observed. Measurements of the free exciton lifetimes reveal varying values in the ps-range depending on the doping concentration of the crystals. With increasing impurity concentration the lifetime decreases, indicating efficient trapping of free excitons by defects forming bound excitons. The lifetimes of the free excitons occur in many cases as risetime of the bound exciton luminescences. At higher excitation intensities an increase of free exciton lifetime is observed, the bound exciton recombination channels saturate.

The dynamical behaviour of the bound excitons under resonant excitation has been investigated by means of pump-and-probe technic. The time constants of the observed saturation are in good agreement with the above mentioned luminescence decay results. It could be shown that even at low excitation intensities a nonlinear behaviour occur due to the saturation of the bound exciton transitions.

Native Defect Compensation in Wide-Band-Gap Semiconductors

D.B. Laks,[a,b,*] C.G. Van de Walle[c], G.F. Neumark[a], and S.T. Pantelides[b]

a. Metallurgy Division, Columbia University, New York, NY 10027
b.IBM T. J. Watson Research Center, Yorktown Heights, NY 10598
c.Philips Laboratories, Briarcliff Manor, NY 10510
* Present address: Solar Energy Research Institute, Golden, CO 80401

Wide-band-gap semiconductors are of great technological interest, but are plagued by one major problem: they can typically be doped either n-type or p-type, but not both. For example, it is comparatively easy to make n-type ZnSe (E_g = 2.7 eV), but extremely difficult to make p-type material. One of the most popular explanations of the source of this problem is compensation by native defects, which claims that placing the Fermi level near the band edge will induce the formation of compensating native point defects. This mechanism has been invoked for more than 25 years, but there is no convincing evidence either for or against it.

We determine the concentrations of all native point defects in ZnSe, using state-of-the-art *ab initio* total energy calculations. These are the first accurate defect calculations for a II-VI semiconductor, and include a correct treatment of the Zn 3d electrons. Careful attention is paid to the effects of lattice relaxations and entropies on our results.

Defect concentrations in a compound semiconductor like ZnSe are stoichiometry dependent. We find that native defect concentrations are too low to cause compensation in stoichiometric ZnSe.[1] Small deviations from stoichiometry can produce enough native defects to compensate doping. However, we find that for either Zn-rich or Se-rich material, native defects will compensate both n-type and p-type doping; thus deviations from stoichiometry cannot explain why ZnSe prefers to be n-type. We have also calculated native defect concentrations in diamond (E_g = 5.4 eV). Here too, we find that there are not enough native defects to compensate doping. In the absence of a generic mechanism, specific dopants should be examined case by case.

This work was supported in part by NSF grant ECS-89-21159 and ONR contract N00014-84-0396.

1. D.B. Laks, C.G. Van de Walle, G.F. Neumark, and S.T. Pantelides, Phys. Rev. Lett. **66**, 648 (1991).

Wednesday Afternoon, 24 July

No Sessions

Session J

Donors in Compound Semiconductors - II

Thursday, 25 July, 9:00 AM

Physics Auditorium

CORRELATION EFFECTS DUE TO IONIZED DEFECTS IN SEMICONDUCTORS

Z. Wilamowski[a], W. Jantsch[b], G. Ostermayer[b] and J. Kossut[a]

[a]Institute of Physics of the Polish Academy of Sciences,
Al. Lotnikov 32/46, 02-668 Warsaw, POLAND

and:

[b]Institut für Experimentalphysik, Johannes-Kepler-Universität,
A-4040 Linz - Auhof, AUSTRIA

Ionized centers in semiconductors are the source of random Coulomb potential fluctuations because of the random spatial incorporation of defects within the host crystal. In general, these fluctuations only cause an effective level broadening. There are, however, two types of situations, in which we encounter some freedom in the spatial distribution of charges among defect states: (i) resonant states and (ii) centers with negative U. In these cases, minimalization of the total Coulomb energy may lead to spatial order in the distribution of charge among the random defect sites. In this paper, we discuss the origin and the consequences of this correlated occupancy for the two examples which have been investigated so far: (i) HgSe:Fe and (ii) DX centers in AlGaAs. Experimental evidence and theoretical models are reviewed.

Iron in HgSe (i) forms a resonant and hence self-ionizing donor state about 200meV above the conduction band edge. As a consequence, the Fermi-level becomes pinned to this state for Fe concentrations exceeding $5 \cdot 10^{18} cm^{-3}$. Additional iron is incorporated in its neutral state. The total Coulomb energy becomes minimum then if the electrons are distributed in such a way among the neutral donors that there are no two ionized donors closer than the "correlation radius" r_c. In other words, we obtain short range order. This ordering manifests itself in an increase of the free electron mobility by a factor of up to three which is a consequence of the suppression of ionized impurity scattering. The donor density of states is strongly broadened and exhibits a Coulomb gap which has been detected in a line-width analysis of EPR experiments.

In their ground state, DX centers (ii) are negatively charged leaving at least (because of compensation) the same number of donors positively charged. Here the total Coulomb energy depends on the spatial distribution of positive and negative charges within the random matrix of donors. Taking the inter-impurity Coulomb interaction into account in a simple "impurity self-screening approach", we show that the activation energy of the free carrier concentration vs. alloy composition, the thermal emission kinetics, the capture kinetics, and the free carrier mobility (both in steady state and and during transients) can be explained in a consistent way. Analysis of the experimental data allows us to construct a general energy diagram of the DX center with respect to the ground state energies (split by different numbers of Al neighbors) and capture- and emission barriers together with their dependencies on temperature, alloy composition and hydrostatic pressure.

Capture Kinetics of the Individual DX Center Levels

Z. Su and J. W. Farmer
Research Reactor, University of Missouri
Columbia, MO 64211, USA

It is well known that both the capture and the emission processes for the DX center are non-exponential. However, most of the earlier work on the DX center did not resolve either process into its components. Recently it has been shown that the emission process of the DX center can be resolved into no more than four components, each of which has a distinct emission energy (i.e.,without any significant broadening). In this paper the question of whether the capture process is simply a superposition of four simple processes described by discrete capture barriers is examined.

The capture process is very broad. In the present work the capture process for the individual levels has been resolved. It is found that the filling of each individual level is still much too broad (three to four decades in time) to be ascribed to a process involving a discrete capture barrier. Therefore, a distribution of capture barrier heights for each level is required to account for the observed width. This finding dismisses the possibility that the very broad capture is due to the sum of four discrete capture barriers. In addition, it is found that the centroids of the distributions of the different levels are not the same, as has sometimes been assumed in previous work.

It is concluded that while the emission process may be determined solely by the local environment (i.e., the number of Al nearest neighbors), the capture process is sensitive to a longer range environment which fluctuates spatially. The fluctuation leads to a distribution in capture barrier heights for each level.

ON THE KINETICS OF PHOTO-CONDUCTIVITY IN AlGaAs:Si

G.Brunthaler, G.Ostermayer, A.Falk and W.Jantsch
Institut für Experimentalphysik, Johannes–Kepler–Universität,
A–4040 Linz, AUSTRIA
and
Z.Wilamowski
Institute of Physics of the Polish Academy of Sciences,
Al. Lotnikov 32/46, 02–668 Warsaw, POLAND

After illumination at low temperature, n–type $Al_xGa_{1-x}As$ exhibits the well known effect of persistent photo–conductivity (PPC). During the heating process, the carrier concentration vs. temperature shows two or three steps, depending on x and the donor concentration (Brunthaler and Köhler, Piotrzkowski et al.). This effect has been attributed to the capture and reemission of electrons from different DX–levels correspondung to different numbers of Al neigbours in the alloy.

We have performed additional experiments on the decay of the light induced photoconductivity on AlGaAs:Si samples at constant temperature, in order to get information on emission and capture barriers. We find highly nonexponential transients. In order to explain these together with the steps in "warming" curves, we consider 3 mechanisms: (i) the variation of the free electron quasi–Fermi level E_F*, during the transients, (ii) the broadening of the capture barriers due to Coulomb potential fluctuations, and (iii) a two stage equilibration process which results from capture across a single capture barrier and reemission across different emission barriers of the alloy split levels.

The quasi–Fermi level E_F* decreases (i) during the capture transient from a degenerate position of up to 60 meV above the conduction band edge in highly doped samples down into the gap. As a consequence, the effective barrier for capture varies also and causes non–exponential behavior. Futhermore we consider the effect of fluctuations in the local potential (ii) due to the positively and negatively charged donors. These Coulomb potential fluctuations are estimated to amount to up to 50 meV for a Gaussian distribution causing a comparable effect in the variation of the effective capture barrier.

Next, we consider capture and reemission (iii) from the four different DX–levels. We consider first the complete statistics, according to which 35 different DX–center types exist, with four distorted states each (T.N.Morgan). The rate equations for the electron transfer between the conduction band and the different levels of all 35 center types are simultaneously integrated numerically within the single donor and the negative U model. We compare the results of the 35 center model with the results of the usually used 4 center model with one distorted site level each.

Finally, we combine the 4 center model with the Coulomb fluctuations. The emission barrier practically is not affected by these fluctuations (i) since emission is an intra–center process. Evaluation of the steps in the quasi–Fermi level during warm–up allows to estimate the alloy splitting of about 60 meV in total. The top of the barrier practically does not depend on the number of Al neigbours (Mooney, Piotrzkowski). Consequently, the capture barriers are not affected by alloy splitting, but the emission barriers are. At low temperature, the different DX–centers thus capture electrons at equal rates which, because of their different ground state energies, leads to a non–thermal population. In a second stage, multiple emission and recapture leads to thermal equilibrium. The time constant in this stage are much longer than in the first one which explains both the strong non–exponentiality of the isothermal transients and the steps in the warming curves.

Session K

EL2

Thursday, 25 July, 10:40 AM

Physics Auditorium

PHOTOQUENCHING AND PHOTORECOVERY OF THE EL2 DEFECT IN n-GaAs UNDER HYDROSTATIC PRESSURE.

Piotr Dreszer
High Pressure Research Center "Unipress", Polish Academy of Sciences, Sokolowska 29/37, PL-01-142 Warsaw, POLAND
Michal Baj
Institute of Experimental Physics, Warsaw University, Hoza 69, PL-00-681 Warsaw, POLAND

Recently we proved that both optical accessibility and electrical activity of the EL2 defect in its metastable configuration (EL2*) must exist jointly and that they are due to the pressure-induced population of the acceptorlike $(EL2^*)^{-/o}$ level of metastable EL2 [1]. Since in n-type GaAs and at high pressure the photon-induced transformations of the EL2 defects between their normal (EL2) and metastable (EL2*) configurations are accompanied by change of their charge state and alter the free electron concentration (negative and positive persistent photoconductivity effects which can be easily monitored by means of electrical conductivity measurements), this gives us unique experimental tool to study the EL2-photoquenching and photorecovery processes. The experiments are performed on two 350µm- and 30µm-thick n-type GaAs samples in the pressure range of 0.3-0.8GPa. For different initial distributions between (EL2) and (EL2*) we investigate at constant pressure and T=5.4K the transients of electrical conductivity of the samples during continuous sweep of irradiating photon flux from a grating monochromator in the spectral range 0.8-1.65eV. A newly developed method based on model of kinetics enables us to numerically extract from experimental data both optical cross sections of the EL2-photoquenching and EL2-photorecovery with high resolution and accuracy.

The photoquenching spectrum consists of broad Poissonian-shaped band (1-1.4eV) on which are superimposed a zero-phonon-line (ZPL) with multiphonon replicas spaced at intervals of 11meV. The ZPL and replicas ride over the onset of vibronic band with increasing pressure similarly as was found for intra-$EL2^o$ absorption spectrum [2]. Any results of our numerical simulation of the vibronic band shape predict the ZPL energetic position well below than the ZPL energy observed at high pressure. This fact strongly supports our previous hypothesis that the two features (ZPL and broad band) could be related to optical transitions to two different final electronic states [2].

The photorecovery spectrum, beside a weakly-dispersive photoionization-like structure, exhibits a very strong and sharp line with a halfwidth of 15meV. The center of the line is positioned 17meV below the energy of band-to-band transitions and it moves with pressure to higher energies with the same pressure shift (105meV/GPa) as that of GaAs energy gap. The maximum efficiency of the photorecovery process is a few times higher than that found for the photoquenching one. Supplementary high pressure measurements of optical absorption of the investigated samples revealed an existence of very strong additional absorption when the EL2 defects were transformed to its metastable configuration - this effect results in substantial shift of the fundamental absorption edge toward lower energies. Based on our experimental findings and referring to As_{Ga} - As_iV_{Ga} theoretical model [3] we discuss plausible mechanism of the photorecovery and suggest that it can be induced under pressure by a capture of photon-created hole at metastable EL2 in its negative charge state $[(EL2^*)^- + h]$ subsequently leading to disappearance of the configuration barrier separating (EL2*) and (EL2) configurations.

[1] M. Baj, P. Dreszer and A. Babinski, Phys. Rev. B 43, 2070 (1991)
[2] M. Baj and P. Dreszer, Mat. Sci. Forum vols. 38-41, 101 (1988)
[3] J. Dabrowski and M. Scheffler, Phys. Rev. B 40, 10391 (1989)

Interaction of EL2 in Semiinsulating GaAs with Above Bandgap Light

K. Khachaturyan, E.R.Weber and J.Horigan
Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA 94720 and Materials Science Division, Lawrence Berkeley Laboratory, Berkeley CA 94720
and W.Ford,
Harris Microwave, 1530 Maccarthy Blvd., Milpitas, CA 95035.

For the first time, photoconductance and photocapacitance characterization of semiconductors was extended to excitation energies above the bandgap. This was achieved by using a microfabricated periodic grating of electrodes of alternating polarity with 20μm period, which have an electric field penetration depth of 3.2μm, comparable to the penetration depth of above bandgap light. Photocapacitance, rf photoconductance and dc photoconductance measurements were used to investigate the interaction of EL2 in semiinsulating GaAs with the above bandgap light. It was found that at 4K even for excitation energies higher than the bandgap, the photocurrent is still dominated by excitation from EL2 and can be optically quenched by illumination with EL2 quenching light. The ratio of the contribution of EL2 to the contribution of band-to-band electron-hole pair excitation decreases with increasing light intensity.

After photoquenching of EL2, intrinsic light with energy greater than 1.63eV could optically recover EL2 from the metastable state at 4K. The results support the model that this optical recovery is a recombination-enhanced defect reaction, triggered by electron capture into an acceptor level associated with the metastable state of EL2. In a two beam experiment, simultaneous illumination with light of a 1mW He-Ne laser reduced the EL2-related photocurrent created by extrinsic illumination, which might be due to the reduced electron lifetime in the presence of photo-excited holes.

The isolated Arsenic Antisite defect and EL2 - an ODMR investigation of electron irradiated GaAs

K. Krambrock, H. Söthe, J.- M. Spaeth
University of Paderborn, Fachbereich Physik,
Warburger Str. 100A, D - 4790 Paderborn, F.R.G.

Semi - insulating (s.i.) GaAs was irradiated with 3 MeV electrons at 4.2 K with a dose of 5 10^{17} cm^{-2}. The sample was held below 90 K. In the optically detected electron paramagnetic resonance (ODEPR) a typical As_{Ga} antisite spectrum is detected with an ^{75}As hyperfine (hf) splitting of 2650 MHz identical to that of $EL2^+$. However, the magnetic circular dichroism of the absorption (MCDA) of this defect shows only a derivative like spectral shape which is part of that known for $EL2^+$. Optically detected electron nuclear double resonance (ODENDOR) spectra show higher ligand symmetry: according to the preliminary analysis they arise from an isolated As_{Ga} defect. In addition some other defects are present, but no EL2 is found. Upon warming up to 330 K the isolated As_{Ga} defect disappears and a new antisite defect is found with the same ^{75}As hf splitting, which can also be produced by e^- - irradiation at 300 K (RT). It has lower symmetry and is an As_{Ga} - pair defect, called As_{Ga} - X_1. A preliminary account of its properties (MCDA, ODEPR, zero phonon line (ZPL) and energy level) was given in [1]. Its ODENDOR analysis is in progress. Again no EL2 is found. From the known energy level of the As_{Ga} - X_1 we know that EL2 originally in the s.i. sample was destroyed upon e^- - irradiation. When warming up to 520 K As_{Ga} - X_1 is destroyed and now EL2 is found with its MCDA, ZPL and ODENDOR spectra and bleaching properties. These results show that the isolated As_{Ga} forms pair defects at a temperature as low as RT. It cannot be identified with the EL2 defect in agreement with earlier ODENDOR measurements which showed that EL2 is an As_{Ga} - As_i pair defect [2]. The results confirm that the As_i is mobile near 500 K [3]. Neither the isolated nor the As_{Ga} - X_1 have the EL2 bleaching properties, theirs are different.

[1] J. - M. Spaeth, K. Krambrock and D. M. Hofmann, 20th Int. Conf. on the physics of semiconductors, ICPS 1990, Thessaloniki, Greece, p.441
[2] B. K. Meyer, D. M. Hofmann, J. R. Niklas and J. - M. Spaeth, Phys. Rev. B 36, 1332 (1987)
[3] D. Stievenard, X. Boddaert, J. C. Bourgoin and H. J. von Bardeleben, Phys. Rev. B 41, 5271 (1990)

THEORY OF THE OPTICAL ABSORPTION AND OF THE MAGNETIC CIRCULAR DICHROISM OF ANTISITE RELATED DEFECTS IN GaAs

Michel LANNOO, Christophe DELERUE and Guy ALLAN
Laboratoire d'Etude des Surfaces et Interfaces, URA 253
CNRS ISEN, 41, blvd. Vauban, 59046 Lille Cedex, France

Antisite related defects like EL2 in GaAs are known to exhibit characteristic optical [1] and MCD spectra [2]. These contain important information concerning the microscopic structure of these defects. The first part of this paper is devoted to an analysis of the zero-phonon line of EL2 [1] whose stress-splitting has been taken as evidence of local T_d symmetry, supporting the identification to the isolated As_{Ga} antisite. Here we explore the possibility discussed in [3] that it corresponds to a transition from a deep donor state to the 1s states derived from the L minima. We first show that, in T_d symmetry, the existence of a deep A_1 donor state leads to an inversion of the A_{1L}(1s) and T_{2L}(1s) combinations of the 1s one valley states. This is confirmed by experiment for the double donor Se in Ge [4]. The same result should hold true for As_{Ga} in GaAs, except that the L derived 1s states are now sharp resonances. In this case one can explain the stress splitting data by considering that each 1s EMT one valley state rigidly follows the corresponding minimum under stress and also understand the origin of the so-called replica. An important consequence is that the initial state of the transition must be + which provides a strong argument against the isolated As_{Ga} antisite.

Another technique is the measurement of the magnetic circular dichroism of the optical absorption (MCDA). A complete theory of the MCDA is still missing for defects in semiconductors. We propose a calculation based on an original Green function formulation. We show how the MCDA can be expressed under a form which allows a direct computation of the spectrum from a Green function calculation of the electronic structure of a point defect. We present an application to the case of a selfconsistent tight binding calculation of the isolated anion antisite As_{Ga} in GaAs in the absence of lattice distortion. Our results show that the MCDA spectrum is dominated by the A_1-T_2 transition between the deep A_1 gap state and the resonant T_2 state in the conduction band. Its characteristic shape differs from what is observed for EL2 or for other antisite related complexes. For EL2 the difference can be ascribed either to strong distortion of the isolated antisite or to compexing with another defect.

[1] M.Kaminska, M.Skowronski and V.Kuszko, Phys. Rev. Lett., 55, 2204, (1985).
[2] B.K.Meyer, J.M.Spaeth and M.Scheffler, Phys. Rev. Lett., 52, 851, (1984).
[3] H.J.von Bardeleben, Phys. Rev. B 40, 12546, (1989).
[4] H.G.Grimmeiss, L.Montelius and K.Larsson, Phys.Rev. B 37, 6916, (1988).

Session L

Hydrogen in Silicon

Thursday, 25 July, 9:00 AM

Perella Auditorium

REORIENTATION OF THE B-H COMPLEX IN SILICON BY ANELASTIC RELAXATION EXPERIMENTS

G. CANNELLI,[1] R. CANTELLI,[2] M. CAPIZZI,[3] F. CORDERO,[4] A. FROVA,[3] A. LO PRESTI,[2]

[1] Dipartimento di Fisica, Università di Perugia, Perugia, Italy
[2] Dipartimento di Energetica, Università di Roma "La Sapienza", Rome, Italy
[3] Dipartimento di Fisica, Università di Roma "La Sapienza", Rome, Italy
[4] Istituto di Acustica "O.M. Corbino", CNR, Rome, Italy

Measurements of elastic energy dissipation and of elastic modulus have been carried out in 10^{19} cm^{-3} B-doped Si samples, before and after ion-gun irradiation with hydrogen. Experiments were performed simultaneously at two widely separated frequencies (2.4 and 31 kHz). The unhydrogenated samples display a monotonic decrease of the dissipation curve between 300 and 60 K, whereas the H-treated ones present, for the two frequencies, peaks at ~125 K and ~145 K, due to a thermally activated relaxation process. The activation energies deduced from both the peak shift with frequency and the peak width have the same value, $E = 0.22$ eV. This indicates that the observed relaxation process is characterized by a single relaxation time, whose pre-exponential factor is $\tau_0 = 8 \times 10^{-14}$ s.

The measured activation energy is in excellent agreement with the theoretical estimate for H trapped in bond-center position between neighboring B and Si atoms [1]. The absence of broadening of the dissipation peak demonstrates that the interaction between the boron trapping centers is still negligible at the present concentration. The measured value of the activation energy is also in agreement with the one estimated from infrared spectroscopy in uniaxially stressed samples [2].

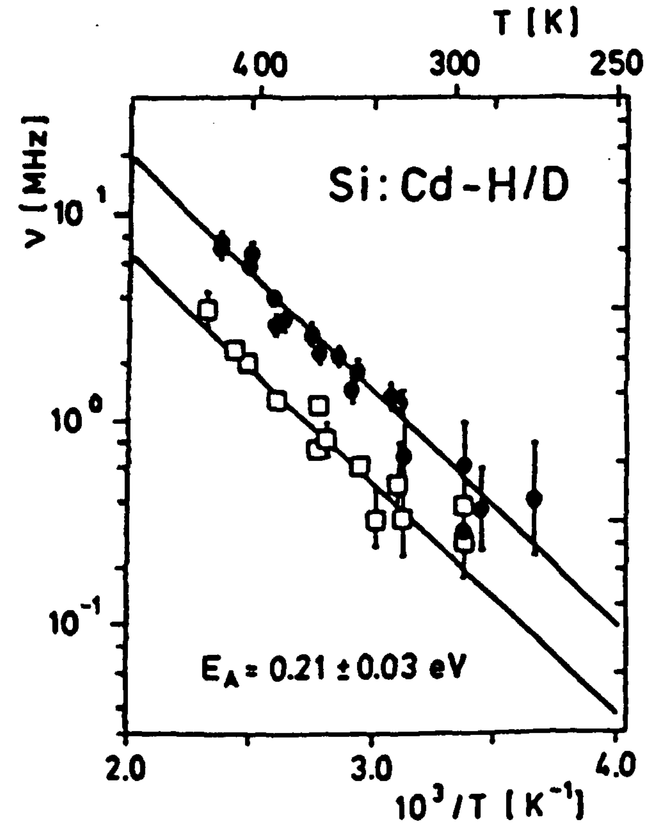
[1] P.J.H. Denteneer, C.G. Van de Walle, and S.T. Pantelides, Phys. Rev. B 39, 10809 (1989).
[2] Michael Stavola, K. Bergman, S.J. Pearton, and J. Lopata, Phys. Rev. B 61, 2786 (1988).

Localized Kinetics of Hydrogen in Cd-H Complexes in Silicon

M. GEBHARD, B. VOGT, and W. WITTHUHN

Physikalisches Institut der Universität Erlangen-Nürnberg, Erwin-Rommel-Str. 1, D-8520 Erlangen, FRG

The locally restricted kinetics of hydrogen and deuterium motion about Cd in Si is studied by Perturbed Angular Correlation Spectroscopy (PAC). Close Cd-H and Cd-D pairs were identified by their characteristic electric field gradients. The kinetics of these complexes was extracted directly from the PAC time spectra. In the temperature region between 270 K and 430 K clear evidence of a thermally activated motion of hydrogen or deuterium about the Cd with an activation energy of 0.21eV for both, hydrogen as well as deuterium has been found. The isotopic mass dependent attempt frequencies are in the order of $10^9\ s^{-1}$, which is orders of magnitude smaller than a typical phonon frequency. The present investigation favours an interpretation in terms of a thermally activated tunneling of hydrogen or deuterium about Cd. The figure shows an Arrhenius plot of ν, where ν is the fluctuation rate of the hydrogen motion (filled circles) or deuterium motion (open squares) about the Cd.



MICROSTRUCTURE OF HYDROGEN AND DOPANTS IN AMORPHOUS Si

James B. BOYCE
Xerox Palo Alto Research Center
Palo Alto, CA 94304 USA

Nuclear magnetic resonance (NMR) has been successfully applied to the study of the microstructure of hydrogenated amorphous silicon and related materials. It has been used to determine the local bonding and structural environment of the host atoms, the hydrogen, and the dopants. Here we review results from NMR measurements designed to obtain information on (1) the H distribution and bonding in hydrogenated amorphous materials and (2) the local bonding structure of dopants in hydrogenated amorphous silicon (a–Si:H). These results for the amorphous systems are then compared and contrasted with what is known for crystalline silicon. First, we review some of the NMR experimental results on the hydrogen microstructure in hydrogenated amorphous semiconductors and compare the results on plasma-deposited a-Si:H, remote–hydrogen–plasma–deposited a–Si:H, thermally annealed a–Si:H, doped a–Si:H, microcrystalline Si and amorphous (Si,Ge):H alloys. A common feature is that these materials exhibit a heterogeneous distribution of hydrogen bonded to the semiconductor lattice in dilute and clustered phases. In addition, the lattice contains voids of varying number and size that contain non-bonded molecular hydrogen whose quantity is altered by deposition conditions and thermal treatment. These results will then be compared with recent work on hydrogen clusters in crystalline silicon. Second, we review some aspects of the local bonding structure of dopants in a–Si:H. A significant fraction of the dopants are found to be in dopant-hydrogen clusters. The detailed structures of these clusters are similar to those proposed to explain hydrogen passivation in crystalline silicon. The similarities of the determined local structures and their implications for the doping efficiency are discussed.

Dissociation and Diffusion of Hydrogen in Boron Doped Silicon

T. Zundel and J. Weber

Max-Planck-Institut für Festkörperforschung,
Heisenbergstr. 1, 7000 Stuttgart 80, Federal Republic of Germany

The dissociation of the boron-hydrogen complex is studied, and an effective hydrogen diffusion coefficient D_{eff} is determined in boron doped silicon for temperatures T in the range from 60°C to 140°C. The values of D_{eff} follow the equation $N_A D_{eff} = P_0 \exp(-E_P/kT)$ with E_P=1.28 eV, $P_0 = 1 \times 10^{20}$ cm^{-1}s^{-1}, and N_A the acceptor concentration. The diffusion process is entirely trap-limited and does not depend on the diffusivity of the free hydrogen. We present a model for the diffusion process which predicts that $N_A D_{eff} = \nu/4\pi R$, where ν is the dissociation frequency of the BH complex and $R \simeq 3.5$ nm the collision radius, which describes the trapping of hydrogen at the boron atom.

NEW TRAPS FOR INTERSTITIAL HYDROGEN IN BORON- AND PHOSPHORUS-DOPED SILICON

L. KORPAS and J.W. CORBETT
Physics Department, SUNY, Albany, NY 12222

S.K. ESTREICHER
Department of Physics, Texas Tech University, Lubbock TX 79409-1051

Recent SIMS and electrical measurements in $p-$ and $n-$type silicon have revealed the existence of new trapping sites for interstitial hydrogen. The concentration of immobilized hydrogen correlates with that of the dopants, suggesting that already passivated dopants may be the trapping centers. We used the approximate *ab-initio* Hartree-Fock method of partial retention of diatomic differential overlap (PRDDO) to explore the potential energy surfaces for complexes involving two interstitial H's and one substitutional B or P. We compared the depths of these new traps for H to traps in intrinsic material (bond-centered H, H_2, and H_2^*). In all these calculations, the host was modelled by clusters of 35 to 44 host atoms, with surface dangling bonds saturated by H atoms.

In $p-$type material, we optimized the geometry for 12 different configurations, each involving up to 15 degrees of freedom. One of the $\{B, H, H\}$ complexes is far deeper in energy (more than 1.0 eV) than any other configuration, including the trapping of the second interstitial H at a bond-centered site far away from the passivated $\{B, H\}$ pair. In the minimum energy configuration, there are *two* $B–H–Si$ bonds. The conformation where B is substitutional and the two H's form an H_2 molecule nearby is over 4 eV above the ground state.

The study of the $n-$type case is still under way. Preliminary calculations on the trapping of H by the $\{P, H\}$ pair strongly suggest that the lowest energy corresponds to the trigonal $P–H–Si–H$ configuration. This trap appears to be even more stable than the most stable $\{B, H, H\}$ one. The conformation where P is substitutional and the two H's form an H_2 molecule nearby is at least 3 eV higher.

In intrinsic material we find the lowest-energy state of two hydrogen atoms to be the H_2^* (or "$H_{AB}H_{BC}$") configuration, preferred by 1.18 eV over the H_2 molecule. However these configurations, as well as two isolated bond-centered interstitials, are at least 3.0 eV higher than the most stable $\{B, H, H\}$ or $\{P, H, H\}$ complexes. This could account for the failure to observe H_2^* by IR absorption.

HYDROGEN-INDUCED PLATELETS IN SILICON: SEPARATION OF NUCLEATION AND GROWTH

N. M. JOHNSON, C. HERRING*, C. DOLAND, F. PONCE,
J. WALKER, and G. ANDERSON
Xerox Palo Alto Research Center, Palo Alto, CA 94304, USA

In addition to the numerous, detailed demonstrations of the ability of hydrogen to passivate defects and impurities in single-crystal silicon, it is also known that hydrogen, diffused into silicon at moderate temperatures, can generate extended structural defects.[1] The defects appear within ~0.1 µm of the exposed surface, are planar in shape, and are aligned predominantly along {111} crystallographic planes. These defects are considered to be unrelated to either plasma or radiation damage because they can be introduced with a remote hydrogen plasma system but not with other remote plasmas such as helium.[2] Thus, it has been proposed that just the chemical reactivity of isolated, interstitial hydrogen can, under certain circumstances, result in the generation of hydrogen-stabilized extended defects in the silicon lattice. However, to date there has been no detailed information on the kinetics of platelet formation and dissociation.

In the present study it is demonstrated that the growth of hydrogen-induced platelets in *n*-type silicon can be controlled independently of the nucleation process. The results demonstrate that platelet formation is suppressed at high hydrogenation temperatures (e.g., > 250°C) specifically as a consequence of the suppression of platelet nucleation and that platelets nucleated at lower temperatures (e.g., 150°C) grow dramatically at these higher temperatures, with nominal diameters approaching 100 nm. Raman spectroscopy reveals at least three Si-H vibrational bands in the range from 2060 to 2140 cm^{-1} that directly correlate with the platelets. The relative intensities of these bands depend on both the donor concentration and hydrogenation conditions, and the bands display different thermal annealing kinetics. A study of hydrogen permeation through the platelet zone is yielding further kinetic information on hydrogen incorporation at platelets.

Platelet generation involves the precipitation of a two-dimensional silicon hydride phase from a supersaturated solution of hydrogen in silicon, with features that are reminiscent of Guinier-Preston zones that appear in certain metallic alloys. Platelets are unique in that growth of the Si-H phase involves a highly anisotropic interaction of migrating hydrogen and platelets which sustains the planar configuration.

* Permanent address: Department of Applied Physics, Stanford University, Stanford, CA 94305.

1 N. M. Johnson, F. Ponce, R. A. Street, and R. J. Nemanich, Phys. Rev. B 35, 4166 (1987).
2 N. M. Johnson, C. Doland, F. Ponce, J. Walker, and G. Anderson, Physica B 170 (1991), in press.

AN ISOTHERMAL PUMPING MECHANISM FOR THE INTRODUCTION OF HIGH HYDROGEN CONCENTRATIONS IN P$^+$ LAYERS IN SILICON

A.D. MARWICK, G.S. OEHRLEIN and M. WITTMER
IBM Research Division, T.J. Watson Research Center, P.O. Box 218, Yorktown Heights, NY 10598

Anomalously high hydrogen concentrations were found in highly-doped p$^+$ layers in silicon following isothermal exposure to atomic hydrogen at elevated temperature. The p$^+$ layers were produced by B or Ga implantation followed by rapid thermal annealing (RTA). A range of implant energies, doses, and hydrogenation temperatures were studied. It was found that hydrogen concentrations of up to 10 times the acceptor concentration were achieved in a sharply-peaked distribution centered on the implant profile, for hydrogenation temperatures of 200°C. At lower temperatures, the hydrogen concentration, and the shape of its profile, was similar to that of the dopant, while at higher temperatures the concentration of retained hydrogen was lower than that of the dopant.

Cross-section electron microscopy of the high-hydrogen layers in Ga-implanted material, in which there are no visible defects after implantation and RTA, showed that large extended defects were induced by the hydrogenation. On detailed analysis the majority of these were found to be intrinsic stacking faults with Burger's vector $1/3(\bar{1}11)$, with a small minority of extrinsic type.

Ion channeling and lattice location showed that the hydrogen atoms in samples hydrogenated at 200°C did not occupy a regular lattice site, in contrast to those introduced at 150°C, which occupied near-bond-center sites. We postulate that the excess hydrogen is associated with the stacking faults.

The observed isothermal pumping of hydrogen into p$^+$ layers can be explained by a mechanism involving the formation of hydrogen clusters by hydrogen ions which segregate into the p$^+$ layer under the action of Coulomb forces. A model of this process will be proposed, and the nature of the clusters will be discussed.

Session M

Theory

Thursday, 25 July, 2:00 PM

Perella Auditorium

Pressure Dependence of Formation and Migration Enthalpies for Atomic Diffusion in Si: Conjugate Gradient Minimization of Total Energy

Osamu Sugino and Atsushi Oshiyama
Fundamental Research Labs. NEC Corporation, Tsukuba 305, Japan

We report parameter-free total-energy calculations for the pressure effects on atomic diffusion in Si. The formation and migration enthalpies of defects and of defect complexes are calculated within the local density approximation using norm-conserving pseudopotentials and well-converged plane-wave basis sets. Both the electronic and geometrical degrees of freedom are optimized using an extremely efficient conjugate gradient method which allows us to manipulate a system with up to 216 atoms in a supercell. The following list is the calculated results for the vacancy (V) migration; we also show here new findings about electronic structure and the geometry of the vacancy.

- A 216-cell calculation of the ideal vacancy shows that the wavefunction Ψ of the deep state extends with striking preference along coplanar chains of atoms in $\{110\}$ planes, as was first pointed out by E. O. Kane. For example, $|\Psi|^2$ at the 5-th neighbor atoms in the chain is $\simeq 1/64$ of that at the vacancy, while it is $< 1/1000$ at other 5-th neighbor atoms. The amplitude is compared with the existing ENDOR data and we find a semi-quantitative agreement.

- A 64-cell calculation shows that the relaxation of the neighboring atoms also shows distinguished preference along the above mentioned chains; e.g. the third neighbor atoms in the chain relax about 0.02Å while relaxation of other third neighbor atoms is more than one order smaller.

- We calculate the potential surface for vacancy migration and find that the lowest energy path for V^{2+} is for one of the four nearest neighbor Si atoms to move straight towards the vacant site, as has been generally believed.

- The migration energy barrier is 0.4 eV for V^{2+}, which linearly decreases with applied hydrostatic pressure P; the barrier height becomes almost zero at $P = 60$kbar. We find that the formation energy of the vacancy, on the other hand, increases with pressure which almost cancels the decrease of migration energy; the activation energy of the self-diffusion (via vacancy mechanism) thus does not change very much.

- There are two Jahn-Teller modes for V^0, tetragonal mode and trigonal mode. The calculated relaxation energy is almost the same; it is 0.20 eV for the tetragonal and 0.18 eV for the trigonal. This explains the unexpectedly small activation energy observed for the bond reorientation.

We also discuss the pressure effects on the diffusion of group V elements (As and Sb) emphasizing the importance of the change in the migration energy.

MANY-ELECTRON EFFECTS IN THE NEGATIVE SILICON VACANCY

Frederick G. ANDERSON and Frank S. HAM, Physics Department and Sherman-Fairchild Center, Lehigh University, Bethlehem, PA 18015;

Gunter GROSSMANN, Department of Solid State Physics, University of Lund, Box 118, S-221 00 LUND, Sweden.

A reinvestigation of Watkins's LCAO-MO model for the negative silicon vacancy (V^-) reveals that this model predicts the form of Jahn-Teller (JT) distortion experimentally observed only if many-electron effects (Coulomb interaction) are taken explicitly into account, and then only if JT coupling to τ_2 modes of distortion exceeds that to ε modes.

For V^-, Watkins's interpretation of the defect symmetry (C_{2v}) observed in EPR is that it is the result of a tetragonal JT distortion (ε mode Q_θ), followed by a weaker distortion (Q_ζ) due to one of the trigonal (τ_2) modes. However, if ε-mode JT coupling exceeds τ_2-mode coupling, as suggested by the tetragonal form of JT distortion observed for the positive vacancy (V^+), theory shows that in the LCAO-MO model for V^- an alternative distortion combining both ε modes Q_θ and Q_ε should provide a lower energy. This distortion has D_2 symmetry, with principal axes for the g-tensor coincident with the crystal's cubic axes, in contrast to what is observed. Only if τ_2-mode coupling, as measured by the corresponding one-electron JT energy $E_{JT}(\tau_2)=2V_T^2/3K_T$ [where $V_T(V_E)$ is the one-electron JT coupling coefficient for $\tau_2(\varepsilon)$ modes and $K_T(K_E)$ the corresponding force constant], exceeds the ε-mode coupling, as given by $E_{JT}(\varepsilon)=V_E^2/2K_E$, does the (Q_θ,Q_ζ) distortion have a lower energy than (Q_θ,Q_ε). However, in this case there is another distortion involving only the τ_2 mode Q_ζ alone that should have an even lower energy, and the unpaired electron would then be equally shared by the four silicon nearest neighbors of the vacancy, again contrary to observation.

In order that the observed (Q_θ,Q_ζ) distortion be the ground state, we find we must have not only that $E_{JT}(\tau_2) > E_{JT}(\varepsilon)$ for V^- but also that electron-electron interaction places the ^2E term of the t_2^3 electronic configuration sufficiently far in energy above the $^2T_1$ term. This requirement imposes a lower bound,

$$U > 9[E_{JT}(\tau_2) - E_{JT}(\varepsilon)],$$

on the intra-atomic Coulomb energy U. An additional constraint,

$$U < [9E_{JT}(\varepsilon) + 3E_{JT}(\tau_2)]/2,$$

is given by the requirement that the JT distortion place the (Q_θ,Q_ζ) minimum below the high-spin singlet term $^4A_2$. The importance of both JT and many-electron effects is therefore demonstrated for V^- in silicon (and similarly for isoelectronic vacancy-like defects such as Pt^-), together with the surprising result that the relative strengths of ε- and τ_2-mode JT coupling for V^- are the reverse of those for V^+.

The portion of this work done at Lehigh University was supported by U.S. Office of Naval Research Grant No. N00014-90-J-1264.

STRUCTURE, DYNAMICS AND STABILITY OF a-Si: AN AB INITIO, LOCAL ORBITAL MOLECULAR DYNAMICS STUDY

David DRABOLD,
Physics Dept., U. Notre Dame, Notre Dame, IN 46556

Peter FEDDERS
Physics Dept., Washington U., St. Louis, MO 63130

Stefan KLEMM
Minnesota Supercomputer Center, Inc., 1200 Washington Ave. So., Minneapolis, MN 55415

We have used the accurate and efficient molecular dynamics (MD) method of Sankey to obtain networks of Si atoms consistent with the experimental radial distribution function and vibrational spectrum of a-Si. These cells have a few percent defect concentration. We discuss both the geometric and electronic structure of these defects in detail. Our cell is found to have a well defined gap, in contrast to the proposed cells with 15% or more defects commonly discussed. In addition, we have studied the structure of Wooten, Weaire and Winer (WWW) and find it to be nearly an energetic minimum according to our bandstructure code. However, relaxing the WWW cell leads to two localized states in the gap. The structures responsible for these are illustrated and discussed.

A general conclusion from our simulations is that there is not necessarily a correlation between the number of coordination defects and localized states in the gap. We find (physically reasonable) structures for which there are both more and less localized gap states than coordination defects.

We use Bayesian spectral analysis to analyze the dynamics (frequency spectrum) of defect structures and compare to "typical atoms" of the structure. The stability of the various defects is discussed.

We have also simulated the structural and dynamical effects of removing an electron from our system. The missing electron comes from a localized state in the gap. MD simulations show that this leads to appreciable structural rearrangements; specifically, to more defects. If this more defective system is then restored to the original charge state, we find that the structure returns essentially to its original configuration.

These observations are consistent with the Staebler-Wronski effect, for which we imagine the missing electron to be photoexcited from a weak bond. The increased number of defects is consistent with the observed efficiency decline in photovoltaics, and the reversibility of the effect is also consistent with experiment.

THEORY OF SECOND-ORDER VIBRONIC REDUCTION FACTORS FOR DEEP LEVEL IMPURITIES IN SEMICONDUCTORS

Colin A. BATES*, Janette L. DUNN*, Victor Z. POLINGER+, Lee D. HALLAM*, Peter J. KIRK* AND Sajida JAMILA*
*Physics Department, The University, Nottingham, NG7 2RD, U.K.
+Institute of Chemistry, Academy of Sciences of the Moldavian SSR, Grosul Str.3, 277028 Kishinev, USSR.

If the orbitally degenerate electronic states of an impurity ion are coupled to vibrations of the surrounding lattice, it is found that the coupling quenches the effect of orbital operators of perturbations such as spin-orbit interaction. This quenching is seen in experiments in the form of reduction factors, with the matrix elements within the new vibronic states being a numerical factor different from the equivalent electronic matrix elements. If the perturbation appears once, such factors are called "first-order". If the perturbation appears twice, "second-order" factors are introduced. In strongly-coupled JT systems, such as magnetic ion impurities in semiconductors, some second-order terms have a larger influence than first-order terms.

A general theory to calculate second-order reduction factors for any degenerate electronic system coupled to any degenerate vibrational system has been developed recently[1,2]. This fully exploits the symmetry properties of the system. Some details of the method will be discussed and new results will be presented for perturbations involving combinations of E- and T_2-type uniaxial stresses within the trigonal ($T \otimes t_2$) and orthorhombic ($T \otimes (e + t_2)$) Jahn-Teller systems. Use will be made of the symmetry-adapted excited vibronic states as derived by Dunn and Bates using an initial unitary transformation followed by an energy minimisation procedure[3]. The results will be illustrated with examples of transition ions in semiconductors.

1. V. Z. Polinger, C. A. Bates and J. L. Dunn; J. Phys.: Condens. Matter 3, 513-27 (1991).
2. Bates C. A., Dunn J. L., Hallam L. D., Kirk P. J., and Polinger V. Z.; J. Phys.: Condens. Matter. 3, (1991) in press.
3. Dunn J. L.; J. Phys. Condens. Matter 1, 7861-81 (1989);
Bates C. A. and Dunn J. L.; J. Phys. Condens. Matt. 1, 2605-16 (1989);
Dunn J. L. and Bates C. A.; J. Phys. Condens. Matt. 1, 2617-29 (1989).

Session N

New Techniques

Thursday, 25 July, 3:50 PM

Perella Auditorium

Combination of Deep Level Transient Spectroscopy and Transmutation of Radioactive Impurities

Manfred Lang and Gerhard Pensl
Institut für Angewandte Physik, Universität Erlangen-Nürnberg,
Staudtstraße 7, D-8520 Erlangen, FRG

Marion Gebhard and Norbert Achtziger
Physikalisches Institut, Universität Erlangen-Nürnberg,
Erwin-Rommel-Straße 1, D-8520 Erlangen, FRG

Michael Uhrmacher
II. Physikalisches Institut, Universität Göttingen
Bunsenstraße 7-9, D-3400 Göttingen, FRG

Deep level transient spectroscopy (DLTS) is a sensitive, defect-specific analysis technique providing the opportunity to evaluate ionization energies, concentrations, and capture cross-sections of deep impurity centres in semiconductors. However, no data are supplied by DLTS regarding the microscopic structure and chemical nature of the observed defects.

In the present paper, it is demonstrated that additional information on the chemical nature and the number of particular probe atoms participating in the investigated defect centre can be obtained by applying deep level transient spectroscopy to radioactive impurities (DLTS-RI). The transmutation of unstable parent nuclei into their stable daughter product leads to a decrease or increase of the measured DLTS peak heights (or defect concentrations) as a function of the decay time of the prevailing radioactive isotope. The method is restricted to such unstable or stable nuclei which create deep, electrically active levels in the band gap of the considered semiconductor. The observed increase of defect concentrations is governed by different formation laws which depend on the number of probe atoms participating in the defect centre. This number of probe atoms can be determined by the fit procedure of the appropriate formation law to the measured defect concentrations.

The DLTS-RI method is demonstrated for p- and n-type Si samples implanted with radioactive $^{111}In^{*}$ which decays into stable cadmium. The Si:$^{111}In^{*}$ system is well suited for the DLTS-RI method because of the favorable value of the indium mean lifetime (τ= 98 h) and the fact that In and Cd form energetically deep acceptors in Si which can be probed by DLTS. We have identified the singly and doubly charged state of the isolated Cd double acceptor in Si ($E^{0/-}= E_V+(487\pm27)$ meV, $E^{-/2-} = E_C-(450\pm20)$ meV) and further one Cd-related complex in B- and Al-doped samples, respectively, with slightly differing energy levels (E(Cd,B1)= $E_V+(200\pm10)$ meV, E(Cd,Al1)= $E_V+(205\pm10)$ meV). Both centres act as single acceptors and contain one Cd atom each. The DLTS-RI method is also used in chalcogen (S,Se)-doped Si samples to investigate chalcogen/In- pairs.

MICROSCOPY OF FRENKEL PAIRS IN SEMICONDUCTORS BY NUCLEAR TECHNIQUES

R. SIELEMANN, H. HÄSSLEIN, M. BRÜSSLER, H. METZNER
Hahn-Meitner-Institut Berlin, Germany

Experiments and techniques are reported which allow the production and subsequent observation of intrinsic defects on an atomic scale. The combination of PAC (Perturbed Angular Correlations of γ-rays) and implantation of nuclear probes at the Berlin heavy-ion accelerator VICKSI offers unique features for this purpose:

First, we have developed a technique which combines PAC with the production of single Frenkel pairs by utilizing the nuclear probe as primary knock-on atom with a monoenergetic recoil energy of about 30 eV. This energy is supplied by neutrino emission of the probe prior to the PAC measurement.

Second, deep implantation in the µm range is employed resulting in low probe concentrations $\cong 10^{14}/cm^3$. With these concentrations experiments can be performed in moderately doped semiconductors without shifting the Fermi level.

We have applied our techniques to Si and Ge and also to the In-containing III-V compounds InP and InSb. The nuclear probe was ^{111}In, in case of the Neutrino-Recoil Experiments the primary probe atom is ^{111}Sn decaying to ^{111}In.

In Ge we have identified the single vacancy in p-type and n-type material, we determine vacancy migration energies and observe correlated recombination of Frenkel pairs. In Si a defect characterized by ν_Q = 28 (2) MHz was observed which has not yet definitely been identified.

Surprisingly, our Neutrino Recoil Experiments in InP and InSb do not result in a measurable defect production despite the fact that 30 eV recoil energy of our ^{111}Sn probe is well above reported threshold energies for Frenkel pair production. We have started to use the nuclear probe ^{116}Sb for recoil experiments which in contrast to the $^{111}Sn/^{111}In$ probe resides on the anionic sublattice which might be favorable for Frenkel pair production.

Modern Muon Spectroscopic Methods in Semiconductor Physics

R.L. LICHTI, C.D. LAMP, Texas Tech. Univ. Lubbock, TX 79409;
S.R. KREITZMAN, R.F. KIEFL, J.W. SCHNEIDER, Ch. NIEDERMAYER, K. CHOW, TRIUMF and University of B.C., Vancouver, B.C. V6T 2A3;
T. PFIZ, MPI fuer Metallforschung, Institut fuer Physik, Stuttgart;
T.L. ESTLE, S. DODDS, B. HITTI, Rice University, Houston, TX 77251;
R. DuVARNY, Emory Univ, Atlanta, GA 30322

The role of the muon in semiconductor physics has been to simulate the behaviour of a light hydrogen defect, and as such, it has played a significant role relating to several central questions regarding hydrogen states in the group IV, III-V and (even) in the I-VII materials. These questions include those regarding electronic structure, site and charge state stability and/or dynamics, and information regarding the motion of a hydrogen-like defect. In this presentation we discuss recently developed integral μSR techniques of muon Level Crossing Resonance (LCR) and muon RF Spectroscopy (RFμSR) since these are both resonance or double-resonance types of experiments that supply highly specific information regarding the electronic structure surrounding the muon defect and its charge state dynamics.

LCR methods in GaAs are used to illustrate how this technique can yield detailed information on the symmetry and magnitudes of the anisotropic Mu*-nuclear hyperfine and electric-quadrupole interactions. This information has unambiguously led to the identification of the low temperature site associated with this state.

RFμSR is illustrated with its use in the determination of muonium charge-state reactions in Si, and Ge. We emphasize that this technique can be used as a *final state* spectroscopy in contrast to conventional time-differential (TD) μSR which is sensitive only to the state populations established during implantation. As such, we present recent work on the μ^+ final state. In Si two distinct temperature regimes are identified, a low temperature one associated with the direct ionization of bond-centered Mu*, and a higher temperature one arising from the ionization of tetrahedral isotropic Mu. Preliminary analysis indicates that the Mu ionization may occur through two channels, a Mu $\leftrightarrow$ Mu* $\rightarrow \mu^+$ process along with the direct Mu $\rightarrow \mu^+$ reaction.

The RF results in Ge sharply contrast those in Si (where as the temperature rises, all the paramagnetic states end up as a μ^+ final state). Here, after the initial low temperature increase, there is a rapid decrease in the μ^+ signal above 230K. This difference suggests a reason for the reduced effectiveness of hydrogen passivation of shallow acceptors in Ge, as compared to Si, since H^+ is considered to be the primary active species (*e.g.*, $B^- + H^+ \rightarrow (B, H)^\circ$ via Coulomb capture).

THE NEW METHODS OF POLARIZED LUMINESCENCE SPECTROSCOPY FOR THE MULTIPARTICLE CENTERS IN SEMICONDUCTORS

S.S.Ostapenko & M.K.Sheinkman
Institute of Semiconductors of Ukrainian Academy of Science,
pr.Nauki 45, Kiev, USSR

The classical polarized luminescence methods are especially elaborated both theoretically and experimentally for the complex luminescence centers (CLC) in semiconductors. The main peculiarity of CLC is that the absorption and luminescence transitions within the center are attributed to different optical dipoles, a and b, with the mutually correlated directions. The physical reasons for this two dipole approximation are given by multiparticle structure of CLC or the lattice relaxation of the center due to photoexcitation. The calculations performed enable to determine the orientations of a and b dipoles in a lattice from the specific polarization diagram curves of the luminescence spectrum and its excitation spectrum. The symmetry of the set of CLC in GaAs, GaP, CdS and ZnSe are evaluated by the methods of polarized luminescence, in some cases the new models of CLC are proposed. The family of metastable EL2 luminecsence centers with different symmetry is found in s.i. GaAs. Some new phenomena attributed to CLC are demonstrated. In particular, the "polarization memory" of thermoluminescence in GaP:N,Cu due to the local lightsum storage is observed and investigated in detail.
The method of the polarization diagrams is extended for the case of the resolved donor-acceptor pairs and applied to selectively excited pairs in AlSb and GaP crystals.

Session O

Dislocations

Thursday, 25 July, 2:00 PM

Physics Auditorium

CHARACTERISATION OF DISLOCATIONS IN THE PRESENCE OF TRANSITION METAL CONTAMINATION

Victor HIGGS*, Edward C LIGHTOWLERS*,
Carl E NORMAN **† and Philip KIGHTLEY***

* Department of Physics, King's College London,
Strand, London WC2R 2LS, UK
** Department of Materials, Imperial College, London SW7 2BP, UK
*** Department of Materials Science, University of Liverpool,
Liverpool L69 3BX, UK
†Present Address : MASPEC Institute, Via Chiavari 18/A, 43100, Parma, Italy

When characterising the electrical and optical properties of dislocations it is important to take into account the impurities decorating them. We have previously shown that dislocations free of transition metal contamination ($< 10^{11}$ cm^{-3})give no measurable EBIC contrast and no dislocation D-band related luminescence, whilst dislocations in material contaminated with low levels of copper ($\sim 10^{13}$ cm^{-3}) show both strongly. In the present work, dislocations produced in high purity FZ silicon and oxidation induced (OISF) and epitaxial (ESF) stacking faults in CVD-grown silicon were intentionally contaminated with Cu, Fe, Ni, Au, or Ag. The effect of contamination was also investigated as a function of concentration.

The as - deformed FZ samples had no observable D-band luminescence and no detectable EBIC contrast. Following deliberate contamination (≈ 0.003 monolayers) the D-band features were observed and the dislocations could be detected by EBIC. The positions of the defect related luminescence lines were virtually identical for the different metals. Very weak (only D1 and D2) or no D-band luminescence was observed from the samples containing either ESF or OISF. After intentional contamination at a low level (≈ 0.003 monolayers) the intensity of the D-band luminescence features increased. For all the defects examined it was found that as the level of contamination was increased above 0.1 monolayers the intensity of the D-band features then decreased until eventually they could no longer be detected.

TEM investigations revealed there were two distinct environments for the defects. When the level of contamination was less than 1 monolayer there was no evidence of precipitation. At higher levels TEM revealed the presence of metal related precipitates along the dislocation lines.

EBIC contrast was observed from all contaminated defects, whether decorated on the atomic scale or by precipitates. As the level of contamination is increased to a degree such that precipitation begins to occur the dislocation related luminescence is lost, suggesting that when precipitates are present, non-radiative recombination dominates.

CORRELATION OF THE D-BAND PHOTOLUMINESCENCE WITH SPATIAL PROPERTIES OF DISLOCATIONS IN SILICON

K. Weronek and J. Weber
Max-Planck-Institut für Festkörperforschung, P.O.Box 800665,
D-7000 Stuttgart 80, Federal Republic of Germany
R. Buchner
Fraunhofer-Institut für Festkörpertechnologie, Paul-Gerhardt-Allee 42,
D-8000 München 60, Federal Republic of Germany
M. Stefaniak and H. Alexander
Universität zu Köln, II. Physikalisches Institut, Zülpicherstr. 77,
D-5000 Köln 41, Federal Republic of Germany
F. Ernst
Max-Planck-Institut für Metallforschung, Seestr. 92,
D-7000 Stuttgart 1, Federal Republic of Germany

Dislocations in Si give rise to a characteristic, low temperature photoluminescence (PL) spectrum. The origin of the so called D-bands is still in debate but low concentrations of residual transition metal impurities (Fe, Cu, Ni) bound to the dislocations are discussed as a possible source for the optical transitions.

We clarified the involvement of impurities in the D-band PL by generating dislocations in high purity wafers taking care to avoid a transition metal contamination during the process. The surface of differently doped Si wafers is locally molten with an Ar-ion laser and subsequently a fast recrystallisation takes place which leads to the formation of dislocations in a surface layer of $\approx 100\mu m$. A strong D-band PL is detected in these samples.

Intentional indiffusion of Cu and Fe causes a decrease of the D-band PL, whereas Ni diffusion leaves the intensity almost unaffected. A further reduction of the residual Cu and Fe contamination in our samples is established by annealing in HCl atmosphere. After this treatment we detect the most intense D1 and D2 bands with the smallest linewidth (0.9meV) ever reported, whereas D3 and D4 exhibit a well resolved fine structure. The fine structure correlates only with the shallow dopants and no influence on the spectrum from transition metals is detected.

The correlation of the D-band PL with the spatial arrangement of the dislocations is established in plastically deformed Si samples. A deformation at 800°C along the [213] crystallographic axis produces predominantly dislocations with Burgers vector along the [011] direction of the $(1\bar{1}1)$ slip plane. The deformed samples are cut appropriately to allow the determination of the intensities and polarisations of the D-bands in different directions with respect to the Burgers vector. A strong intensity difference as well as strong polarisation is detected for D1, D2 and D3, D4 for the emission in different directions. All the properties of the D-bands are directly correlated to the spatial arrangement of the dislocations.

We propose a model for the recombination processes at dislocations in Si and correlate certain PL features with details of the dislocations determined by Transmission Electron Microscopy.

PHOTOLUMINESCENCE AND ELECTRONIC STRUCTURE OF DISLOCATIONS IN *Ge* AND *Si* CRYSTALS

Yuri T.REBANE and Yuri G.SHRETER
A.F.Ioffe Physical-Technical Institute, Academy of Sciences, 194021 Leningrad, USSR

An important property of dislocations in crystals which does not depend on their core structure and extent of decoration by impurities are the long-range dislocation strain fields. Recently we have shown that the 1d-bands split off by these fields from the edges of the corresponding volume bands are a basis for the dislocation electronic structure.Core structure defects and impurities present at a dislocation result in an efficient "doping" of the latter different from that of the host crystal. This doping determines the Fermi level and carrier concentration in the 1d-bands, as well as the carrier transport parameters, such as mobility, lifetime etc. Such an approach permits classification of a dislocation luminescence line according to the magnitude of the squared Burges vector **b**, since the 1d-band splitting energy is proportional to $\mathbf{b}^2$ and is determined by the actual dislocation type. In the present report this concept is being developed not only for describing the dislocation-related luminescence but also for the interpretation of experiments on microwave conductivity, piezospectroscopy and electric-dipole spin resonance (EDSR). The D4-line in *Si* and the $\hbar\omega$=0.513 eV line in *Ge* are shown to be emitted by dislocation excitons which are bound to a 90°-Shockley partial contained in a 60°-dislocation. The luminescence line series in crystals containing dislocations with a different set of stacking fault width can be accounted for by the strain field of a 30°-partial acting on the dislocation exciton energy. The D1 and D2 lines in *Si* have been found to correspond to the emission of dislocation exciton at Lomer-Cottrell dislocations and the partial Frank dislocation, respectively. The luminescence spectra of such microdefects as type A,B,D swirls in *Si* are obtained and shown to be due to the dislocation bounding the microdefects.The possibility of passivation of the core structural defects by transition metal impurities is discussed. The luminescence line splitting under uniaxial compression is found to be 4-for the Frank dislocations, 6-for the Lomer-Cottrell type and 24 for the conventional 60°-dislocations. A theory of EDSR is developed capable of explaining the appearance of the 24 EPR lines and the *g*-tensor symmetry in the experimental EPR study by E.J.Pakulis and C.D.Jeffries. Phys.Rev., 47, N 25, 1859 (1981) of 60°-dislocations in *Ge*.

Characterization of Point Defects in Si Crystals by Highly Spatially Resolved Photoluminescence

Michio Tajima*, **Hiroshi Takeno**** and **Takao Abe****
**Institute of Space and Astronautical Science, Yoshinodai, Sagamihara 229, Japan*
***Shin-Etsu Handotai, Annaka, Gunma 379-01, Japan*

Vacancies and interstitials play a key role in the oxygen precipitation process in Czochralski(CZ)-grown Si crystals. Despite many efforts to measure them directly, none has yet been successful. Edge-type dislocations are known to act as both sinks and sources for the point defects. As a result, anomalous oxygen precipitation occurs in the vicinity of the dislocations after annealing.[1)] The purpose of this study is to visualize the distribution of the point defects by photoluminescence (PL) mapping technique. We have observed for the first time the microscopic distribution around dislocations of both band-edge and deep-level emissions at room temperature. The association of the deep-level emission with the point defects is discussed.

A growing ingot was detached from the melt in order to freeze-in point defects; slip dislocations were introduced during this process. A wafer was sliced from the ingot and annealed at 1000°C for 16 h. Dislocations were revealed by X-ray topography. PL mapping with a spatial resolution down to 1 μm was performed at room temperature.

A PL spectrum of the as-grown crystal consists of band-edge emission at 1.09 eV and deep-level emission at 0.76 eV. The intensity of the 0.76 eV band is raised along the dislocation lines with a width of about 20μm. This core region is surrounded by a characteristic low-intensity region about 100μm wide (denuded zone). The outer background region shows the highest intensity. A complementary intensity profile is observed for the 1.09 eV emission. After the annealing, the core and denuded regions are extended to about 40 and 200μm, respectively.

The results rule out the association of the 0.76 eV band with dislocations and oxygen precipitates. We conclude that the deep levels responsible for the 0.76 eV band are due to vacancy-related secondary defects. Excess vacancies are frozen-in during the cooling process. The characteristic intensity profile for the 0.76 eV band can be explained by the absorption of vacancies by dislocations: this is evidenced by the retardation of oxygen precipitation in the denuded zone. The complementary intensity contrast for the 1.09 eV band is due to the consumption of excited carriers at the deep levels.

1) H. Harada, T. Abe and J. Chikawa: *Semiconductor Silicon 1986*, p. 76.

Session P

Superlattices

Thursday, 25 July, 3:50 PM

Physics Auditorium

SOLID STATE PROCESSES AT THE ATOMIC LEVEL

A. Ourmazd
AT&T Bell Labs, Holmdel, NJ 07733

Many solid state processes involve the substitution of certain atoms on the lattice with other, chemically different species, leaving the structure essentially unaltered. Until recently therefore, the Transmission Electron Microscope (TEM), perfected as a structural probe, has been ineffective in revealing the atomic details of a large variety of solid state reactions. This, and its qualitative nature have restricted the role of electron microscopy to the examination of extended defects, leaving point defects and their reactions inaccessible to direct microscopic examination.

Chemical lattice imaging [1], however, is a TEM based technique capable of revealing changes in the sample *composition* with atomic column resolution. The application of recently developed vector pattern recognition algorithms [2] to chemical lattice images allows the composition of individual atomic columns to be determined with near-atomic sensitivity; single- and double- atom substitutions in individual atomic columns of typical semiconductors can be detected at $\sim 1\sigma$ (70% confidence) and 2σ (90% confidence) levels, respectively. "Chemical Mapping" is thus a quantitative means for studying microscopic changes in the composition of materials, at the atomic level.

It is thus possible to measure interdiffusion coefficients as small at $10^{-22} cm^2/s$ in regions as small as $10^{-19} cm^3$ in volume. Such measurements reveal a host of unexpected phenomena: highly nonlinear interdiffusion, the dominant effect of the surface in determining layer and device stability, exotic forms of chemical relaxation in highly inhomogeneous solids [3]. Equally important, chemical mapping techniques allow one to repeat the early experiments of high energy physics in the solid state. Just as a stack of photographic emulsion layers can be used to track the passage of cosmic radiation, the intermixing at a series of chemical interfaces (such as GaAs/AlAs) can be used to record the arrival and passage of point defects, be they high energy implanted ions, or low energy native point defects injected during an anneal. The sensitivity of chemical mapping allows one to study such processes long before steady-state has been reached, providing access to hitherto unexplored regimes. Finally, it is now possible to use multilayers as microscopic laboratories, in which selected defects may be trapped and interrogated. I will show that the combination of "designer multilayers" grown by modern epitaxy and quantitative chemical microscopy has led to the realization of a number of hitherto Gedanken experiments.

REFERENCES

1. A. Ourmazd, D.W. Taylor, J. Cunningham, and C.W. Tu, Phys. Rev. Lett. **62**, 933 (1989).
2. A. Ourmazd, D.W. Taylor, M. Bode, and Y. Kim, Science **246**, 1571 (1989).
3. Y. Kim, A. Ourmazd, M. Bode and R.D. Feldman, Phys. Rev. Lett. **63**, 636 (1989).

Theory of Zn-Enhanced Disordering in GaAs/AlAs Superlattices*

Q. Zhang, C. Wang, and J. Bernholc
Department of Physics, North Carolina State University
Raleigh, NC 27695-8202, USA.

Although GaAs/AlAs superlattices are quite stable at high temperatures, diffusion of Zn through the superlattice structure leads to disordering of the group III sublattice at temperatures as low as 500 °C. Furthermore, the disordering occurs only in those parts of the sample where Zn is present, indicating that it cannot be explained by Fermi level effects alone.

We have used the quantum molecular dynamics method to examine theoretically several mechanisms of Ga motion in the presence of Zn impurities. We find that the Zn_{Ga}-Ga_I pair in GaAs has a substantially lower formation energy than the isolated Ga interstitial. The low formation energy of this pair results in the interstitial kick-out mechanisms having much lower activation energies than the ones involving vacancies or the dissociative (Frank-Turnbull or Longini) mechanism. The lowest energy path for the interchange of group III atoms involves a kick-out of Zn by a Ga interstitial, followed by Zn diffusion and a subsequent ejection of another group III atom into the interstitial channel. The activation energies for these processes were determined by following the kick-out trajectories and including a full relaxation of all atoms.

In p-type AlAs, the Zn_{Al}-Al_I pair is even more stable than the Zn_{Ga}-Ga_I pair in GaAs. Since Zn diffusion in GaAs is much slower than in AlAs, it is the rate-determining step in the disordering process. The above mechanism provides an explanation of the Zn-induced enhancement without the need to invoke kinetic effects.

* Supported by ONR, grant number N00014-89-J-1827.

Spatial Partition of Photocarriers Trapped at Deep Level Defects in Multiple Quantum Well Structures

D. D. NOLTE and Q. WANG, Department of Physics
M. R. MELLOCH, School of Electrical Engineering
Purdue University, West Lafayette, IN 47907

Photocarriers generated in multiple quantum well structures experience spatially different dynamics, depending on whether they are in the well regions, or the barrier regions. Selective choice of bandgaps and optical excitation wavelengths controls where and how photocarriers trap at defects. This degree of control can isolate specific processes for detailed study, such as photocarrier generation, transport and trapping. Photocarriers that are generated exclusively in the wells are not restricted to trapping at defects in the well regions. The confined carriers can tunnel into the barriers, or overcome them by thermionic emission, and trap into highly localized deep defect states in the barrier regions. These transport mechanisms partition the carriers between barriers and wells, generating trapped space-charge. The charge separation can be easily monitored because the space-charge electric field can be detected via optically-induced changes in the refractive index of the material, called the photorefractive effect.

We have studied photocarrier trapping at defects in proton-implanted semi-insulating GaAs/AlGaAs multiple quantum well samples. The implant damage produces defects that pin the Fermi level near midgap. Internal space-charge fields are generated by illuminating the samples with two coherent pump laser beams that generate photorefractive gratings. The gratings diffract a probe laser, giving a sensitive means to monitor the internal space-charge.

Carrier partition between the wells and barriers can occur under various conditions. We describe two such conditions that lead to dramatic space-charge and electro-optic effects:

a) When the pump photon energy exceeds the barrier bandgap, photocarriers are generated throughout the multiple quantum well structure. A probe laser tuned near the quantum-confined exciton absorption, however, generates carriers only in the quantum wells. This competition gives a direct measure of the carrier transport from the wells into the barriers, where the carriers trap at defects.

b) Electrons and holes have different tunneling and emission rates. The carriers trapped in defects in the barriers will therefore be segregated, with electrons transporting farther into the barriers than the holes prior to trapping. We provide evidence for excess trapped electron densities in the bright interference fringes of pump laser beams tuned to the excitonic absorption.

These results introduce a spectroscopy for a new class of phenomena based on charge separation and trapping at defects in spatially inhomogeneous multilayer structures. Potential applications include devices for optical imaging and computing.

DYNAMICS OF EXCITON CAPTURE, EMISSION AND RECOMBINATION PROCESSES AT SHALLOW DONORS AND ACCEPTORS IN CENTER-DOPED AlGaAs/GaAs QUANTUM WELLS

C I Harris and H Kalt,
Max Planck Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany

B Monemar, J P Bergman and P O Holtz,
Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden

M Sundaram, J L Merz, and A C Gossard,
Center for Quantized Electronic Structures (QUEST), University of Santa Barbara, Santa Barbara, CA 93016, USA

The various processes determining the occupation of free exciton (FE) states and bound exciton (BE) states associated with shallow (Si) donors or (Be) acceptors in AlGaAs/GaAs quantum wells (QW's) have been studied with the aid of timeresolved picosecond (ps) transient photoluminescence (PL) spectroscopy. The samples were 50 period multiple QW's with the doping selectively placed in the mid 20% of the QW. Various doping levels have been used, but a typical value was 10^{10} cm^{-2} for each QW. The QW width d was also varied between 50 Å and 150 Å for different samples. Tunable ps laser excitation with about 5 ps pulses was used for the transient studies, and the temporal response of FE and BE emissions were recorded with a streak camera with a temporal resolution of about 10 ps. The clearest information is obtained with excitation resonant with the FE and the BE, respectively. At high initial exciton densities (10^{10} -10^{11} cm^{-2} per QW) strong interaction processes (both elastic and inelastic) are observed between FE's and BE's, and these processes dominate the initial 100-200 ps of the temporal response. At lower initial exciton densities ($<10^9$ cm^{-2}) the main features of the temporal response can be well accounted for by a standard model of trapping and re-emission of excitons, analogous to the case of bound exciton kinetics in bulk. An extensive theoretical model has been developed and analysed using a computer program which allows us to fully simulate the dynamic excitonic response of the doped QW, as a function of temperature. Examples of the characteristic physical parameters for exciton capture, emission and recombination will be given for different samples. The influence of FE capture into localized excitonic states due to well width fluctuations, as well as the influence of the internal BE electronic structure on the observed BE transients, will be discussed.

Session Q

Hydrogen in Compound Semiconductors

Friday, 26 July, 9:00 AM

Physics Auditorium

Acceptor Passivation in GaP by Positively Charged Hydrogen Manifested by Donor-Acceptor Pair Luminescence

Yasunori Mochizuki and Masashi Mizuta

Fundamental Research Laboratories, NEC Corporation,
34, Miyukigaoka, Tsukuba, Ibaraki 305, Japan

The effect of Coulomb potential on the hydrogen diffusion and resultant neutralization of Zn-acceptors in GaP was studied by photoluminescence spectroscopy. By monitoring the Zn-related donor-acceptor-pair (DA-pair) emission, the degree of intensity reduction after hydrogen passivation for individual pair lines was evaluated. The main finding is that lesser degree of intensity reduction was encountered for closer pairs, for which hydrogen coordination to a Zn atom is obstructed by the presence of a closely located donor atom. The important consequence of such a sensitivity of the hydrogenation process in Coulombic field is that the major portion of hydrogen diffuses in a positive charge state in GaP.

The original sample showed a S-Zn DA-pair emission which consists of a broad band corresponding to remote pairs with separations up to about 40Å and a series of sharp lines due to more closely spaced pairs. After hydrogenation, the sharp line part became apparently more intense than the broad band. This observation suggests that the passivation by hydrogen is less efficient for Zn atoms whose distance to its nearby donor atom is smaller. Furthermore, even the change in the broad band intensity after hydrogenation was found to be smaller than what is predicted from a model calculation combined with the result of electrical measurements, thereby indicating a still detectable effect of Coulomb potential due to a nearby donor. A consistently extrapolated result was further obtained for the nearest neighbour Zn-O isoelectronic center. The intensity reduction of its luminescence was almost negligible as compared to that for DA-pair emission of isolated Zn and O, being parallel to our previous result for nitrogen isoelectronic center.

The suggested charge state of H^+ during diffusion is similar to the case for Si, in which the space-charge technique has been used to determine the charge state. The present observation is complementary in the sense that what we observe is the charge state of hydrogen during the H-Zn defect formation instead of dissociated hydrogen atoms.

CARBON-HYDROGEN INTERACTION IN III-V COMPOUNDS

B. CLERJAUD, D. COTE, F. GENDRON, W-S. HAHN, M. KRAUSE, C. PORTE
Acoustique et Optique de la Matière Condensée
Université Pierre et Marie Curie, Boite 86
F-75252 Paris, cedex 05, France

and

W. ULRICI
Zentralinstitut für Elektronenphysik,
O-1086 Berlin, F.R. Germany

In p-type GaAs and GaP, carbon and hydrogen have a strong tendency to attract each other and form carbon-hydrogen complexes. It is shown that the carbon-hydrogen interaction is dependent upon the position of the Fermi level which allows an estimate of the "isolated" hydrogen donor level in these two materials.

In GaAs, the stretching local modes of vibration (LVM) of the carbon hydrogen complex are sufficiently sharp for performing three types of experiments :

i) Experiments under uniaxial stress show that the carbon-hydrogen complex has a trigonal symmetry.

ii) Reorientation experiments show that a 0.5 eV energy is required for the complex to reorient from one of its trigonal equilibrium position to an other equivalent one.

iii) The study of the temperature dependence of the stretching LVM of the carbon-hydrogen complex allows to evidence its coupling with various specific lattice acoustic phonons giving a deep insight into the dynamical couplings between the C-H bond and its surrounding atoms.

This set of complementary results allows a detailed model of the C-H complex to be sketched.

HYDROGEN-DOPANT INTERACTIONS IN III-V SEMICONDUCTORS.

Jacques CHEVALLIER (a) and Bernard PAJOT (b)
(a) Laboratoire de Physique des Solides de Bellevue, CNRS, 92195 MEUDON Cedex (France)
(b) Groupe de Physique des Solides, 2 place Jussieu, 75251 PARIS Cedex 05 (France)

Hydrogen diffusion in III-V semiconductors usually leads to a reduction of the active dopant concentration and an increase of the free carrier mobility. It is considered that this neutralization of the dopants is the result of the formation of the complex including hydrogen and the dopant atom. The microscopic structure of the complexes is described from a detailed analysis of the infrared local vibrational modes of hydrogen and the dopants. It is shown that the modeling of deuterium diffusion profiles can provide physical parameters such as the electronic level position of hydrogen in the band gap and the thermal dissociation energy of hydrogen-dopant complexes. The results of a new investigation of the hydrogen diffusion profile in $Ga_{1-x}Al_xAs$ alloys as a function of the Al fraction is also presented which opens new possibilities to achieve information on the electronic properties of hydrogen.

INTERACTION OF H WITH IMPURITIES IN SEMICONDUCTORS

R. JONES, S. OBERG[1] and A. UMERSKI
Department of Physics, University of Exeter, EX44QL, UK
[1]Department of Mathematics, University of Lule, Lule, S95187, Sweden

The interaction of H with impurities in semiconductors leads to several distinct effects: firstly, it can passivate electronically active impurities by forming complexes, and secondly it can catalyse atomic processes. The structures of the H-complexes can be calculated by ab initio theory but, experimentally, often only their localized vibrational modes and reorientation energies are known.

The problem from a theoretical point of view is then to calculate these modes and energies. We describe how this can be accomplished using local density functional methods applied to large atomic clusters, and illustrate this with the passivation of the carbon acceptor in GaAs, and the effect of H on the reorientation energy of bond centered O in Si. There are several features of the carbon-hydrogen complex which arise from the calculations which are quite distinct from those of other passivated impurities.

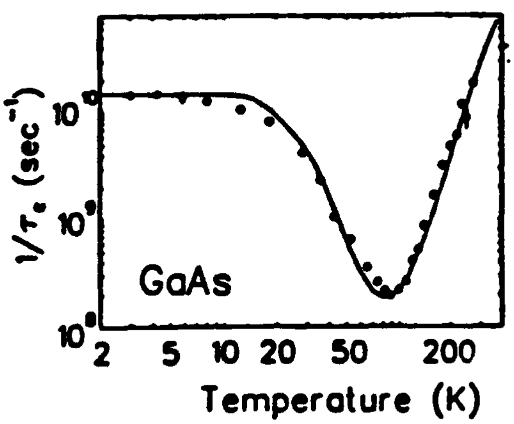
In the case of interstitial oxygen, the calculations show that a weak bond with hydrogen is converted into a strong one during the migration process, hence lowering the O_I migration energy by a factor of two.

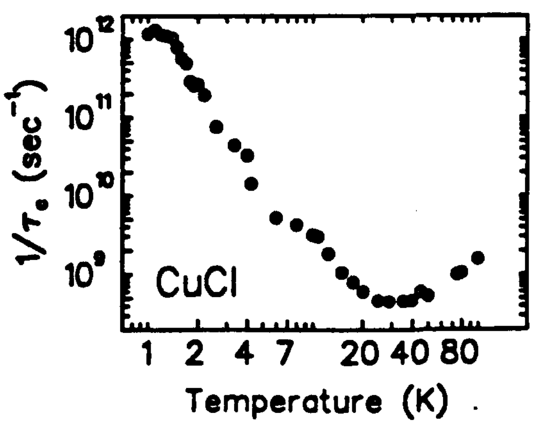
Quantum Motion of Muonium in GaAs and CuCl

J.W. SCHNEIDER*, R.F. KIEFL, J.H. BREWER, K. CHOW, S.R. KREITZMAN, Ch. NIEDERMAYER, T. PFIZ** and T.M. RISEMAN, TRIUMF and Univ. of B.C., Vancouver, Canada V6T2A3; R. KADONO, Institute for Physical and Chemical Research, Wako, Saitama 351-01, Japan; S.A. DODDS and T.L. ESTLE, Rice Univ., Houston, TX 77251; R.C. DUVARNEY, Emory Univ., Atlanta, GA 30322; R.L. LICHTI, Texas Tech Univ., Lubbock, TX 79409; C. SCHWAB, Centre de Recherches Nucléaires, 67037 Strasbourg, France. S.F.J. COX, Rutherford Appleton Laboratory, Oxon, OX11 0QX, U.K.; E.J. ANSALDO, Univ. of Saskatchewan, Saskatoon, Canada S7N0W0; E.E. HALLER, Lawrence Berkeley Laboratory, Berkeley, CA 94720.

In semiconductors muon spin rotation and muon level-crossing resonance provide detailed information on the hyperfine interactions and electronic structure of isolated muonium centers which are closely related to that of isolated atomic hydrogen. Using the related technique of muon spin relaxation, it is possible to obtain complementary information on dynamical processes such as diffusion. Due to the much lighter muon mass ($m_\mu \simeq \frac{1}{9} m_p$) interesting quantum mechanical effects such as tunneling and coherence are expected to be enhanced relative to hydrogen. From the measured spin relaxation of muonium one is able to derive an average correlation time τ_c for fluctuations in the nuclear hyperfine field exerted on the unpaired electron of muonium as it moves from site to site. The figures below show $1/\tau_c$ for isotropic muonium in GaAs (left, from R. Kadono *et al.*, Hyper. Int. 64 635 1990) and in CuCl (right). In GaAs, isotropic muonium is believed to be moving rapidly between interstitial T sites, while in CuCl, there is evidence the muonium undergoes local tunneling around a T site. One of the most interesting features about muonium diffusion is the observed crossover from thermally activated motion at higher temperatures to quantum mechanical tunneling at lower temperatures. This is evidenced by the minimum in $1/\tau_c$ at about 90 K in GaAs and 30 K in CuCl. The nature of the quantum motion of muonium at very low temperatures, where one expects coherent band-like propagation, is still under investigation. In this paper we will discuss and compare the latest results on muonium motion in the two semiconductors; emphasizing the low-temperature regime where now measurements have been extended down to below 1 K.

*Work partially supported by the Swiss National Science Foundation. **Present address: Max Planck-Institut für Metallforschung, D-7000 Stuttgart 80, FRG.





Effects of Reverse Bias Annealing on Hydrogenated Ti/n-GaAs Schottky Barrier Diodes

S. X. Jin, M. H. Yuan, L. P. Wang, and Y. Q. Jia
(Department of Physics, Peking University, Beijing 100871, P.R. China)
G. G. Qin
(Department of Physics, Peking University, Beijing 100871, and International Center for Materials Physics, Academia Sinica, Shenyang 110015, P.R. China)

It was found that due to hydrogenation the Schottky barrier height (SBH) of the Ti/n-GaAs Schottky barrier diodes (SBD) decreases from 0.76eV to 0.58eV and the effective Richardson constant A^{**} from 11 $A/cm^2/K^2$ to 0.03 $A/cm^2/K^2$. We have shown for the first time that the SBH of a hydrogenated Ti/n-GaAs Schottky barrier diode can be controlled by the bias of the reverse bias annealing (RBA) at 100 °C . The larger the bias, the higher the SBH. When the reverse bias is larger than a critical value, 3V in our case, RBA can remove the effect of hydrogenation, i.e. the SBH of a hydrogenated SBD will approach 0.74 eV, the SBH of the control diode without hydrogenation. Annealing without bias can be used to recover the hydrogenated state of the Ti/n-GaAs SBD and the SBH reduces to be 0.58 eV. The experimental results indicate that the behavior of hydrogen near the Ti/n-GaAs interface can be controlled by RBA and the state of hydrogen is reversible. Which is very different from behavior of hydrogen in the bulk of GaAs, where the state of hydrogen is unreversible. A theoretical model, that there are two configurations of hydrogen near the Ti/n-GaAs interface and that only one of them has an effect on the interface state and then on the SBH, is suggested to explain the experiments.

Structure and Stability of Cadmium-Defect Complexes in III-V-Compounds formed after H_2 Plasma Treatment

A. Baurichter, M. Deicher*, S. Deubler, D. Forkel, and W. Witthuhn

Physikalisches Institut der Universität Erlangen-Nürnberg, D-8520 Erlangen, Germany,

ISOLDE Collaboration, *CERN, CH-1211 Geneve, Switzerland*

**Fakultät für Physik, Universität Konstanz, D-7750 Konstanz, Germany*

Exposure of cadmium implanted GaAs, InAs, GaP, InP, and InSb samples to a hydrogen plasma leads to the formation of Cd-defect complexes in these materials /1/. The structure and stability of these complexes have been investigated by means of the Perturbed Angular Correlation Spectroscopy (PAC). The experiments were performed at the ISOLDE facility at CERN, where undoped III-V-compound samples were implanted by 60 keV $^{111m}Cd^+$ ions to doses of $10^{11}...10^{12}$ cm^{-2}. After rapid thermal annealing (GaAs, InAs, GaP, InP) or furnace annealing in sealed quartz ampoules (InSb) the specimens were exposed to a parallel plate dc H_2 glow discharge (30min at 400...500 K). The analysis by PAC revealed the formation of Cd-defect complexes with similar structural properties in all compounds. As a common feature, all configurations are characterized by axially symmetric electrical field gradients, oriented in <111> lattice directions. The hyperfine interaction frequencies (ν_Q) scale approximately with the inversed cube of the lattice constants of the various compounds. These correlations indicate, that the same defect is trapped by the Cd impurity. An additional Cd-defect complex was found in the arsenides. Isochronal annealing experiments show, that both complexes in GaAs anneal at the same temperature, whereas a metastable annealing behaviour is detected in InAs. The stability of the configurations observed in GaAs coincides with the stability of Zn-H pairs in GaAs /2/. The complex formed in InP anneal at significantly higher temperatures. The results can be consistently interpreted by assigning the complexes to cadmium-hydrogen pairs in the bond center configuration with hydrogen bonded to the Group V atoms.

/1/ A. Baurichter, M. Deicher, S. Deubler, D. Forkel, H. Plank, H. Wolf, and W. Witthuhn, Appl. Phys. Lett. 55 (1989), 2301

/2/ A.W.R. Leitch, Th. Prescha, M. Stutzmann, Proceedings of the E-MRS Fall Meeting Strassbourg 1990 (to be published)

Session R

Strained Layers

Friday, 26 July, 9:00 AM

Perella Auditorium

Strain Relief in Thin Films: Can we control it?

F.K. LeGOUES
IBM Research Division, T. J. Watson Research Center
P.O. Box 218, Yorktown Heights, NY 10598

Strain and strain relieving defects play a considerable role in determining the electronic properties as well as the microstructure of epitaxial layers. Strain can be used in technology to manufacture materials with specific properties — e.g. change the band gap in very thin Si/Ge superlattices, but must be understood and controlled in order to obtain the desired properties reproducible. Although we can now grow strained layers of a different lattice parameter than the substrate by keeping them under a certain "critical thickness", it has become apparent that applications requiring strain relieved films will be significantly more difficult to achieve. This is because very little is known, and less is understood, about the nucleation of dislocations in thin films, and in particular, about the formation of threading dislocations.

In this talk, I will discuss several experiments which tackle the questions of the importance of the growth morphology on the introduction, and microstructure, of strain relieving defects, and show that the nucleation of dislocations is the critical step in determining, and controlling, the formation of defects.

In the first experiments we will discuss, the growth of Ge on Si(001) and Si(111) was changed from islands to layer-by layer by using a surfactant. This has dramatic effect on the nucleation of defects. Indeed, in the Ge/Si(001) system, the nucleation of dislocation is suppressed and novel V-shaped defects are formed. For the Ge/Si(111) system, the same dislocations are formed both during islanding and layer-by-layer growth. But layer-by-layer growth forces dislocations to nucleate at the surface as partials, which are later annihilated by the glide of a second partial, resulting in a perfect, relaxed Ge film.

In the second part of the talk, I will discuss the anomalous strain relaxation observed in compositionally graded layers of SiGe/Si(001). In this case, a novel, Frank-Read type, of dislocation nucleation is observed which results in dislocations being injected deep into the Si substrate, leaving the film itself defect free. We will discuss the mechanisms involved and show that this method has been used to grow relaxed, defect free SiGe alloys of arbitrary thickness and composition.

COMPOSITION MODULATION EFFECTS ON THE GENERATION OF DEFECTS IN $In_{0.55}Ga_{0.45}As$ STRAINED LAYERS

F. Peiró, A. Cornet, A. Herms, J.R. Morante
LCMM. Dept. Fisica Aplicada i Electrònica. Diagonal, 645. Barcelona 08028.
S. Clark, R.H. Williams
Dep. of Physics. Univ. of Wales. PO Box 913. Cardiff, UK.

One of the most important concerns in semiconductor heteroepitaxy is the formation of dislocations and similar defects as a result of misfit stresses. It has been demonstrated that these misfit dislocations are favourable sites for controlled gettering of metallic impurities below active device structures. On the other hand, the epithreading dislocations running up and through the layer from the end of misfit dislocations can degrade device performance, particularly if the dislocations are decorated. For some device purposes, therefore, it is better to have a high density of misfit dislocations and a low density of epithreading dislocations. In order to perform defect engineering with misfit dislocations it is clearly important to understand their nucleation, propagation and properties. Unfortanely, the mechanisms that operate to nucleate, multiply and propagate dislocations depend in many cases on the heteroepitaxial system under consideration; especially the degree of misfit, growth temperature and growth mechanism.

In this work, we present the influence of the presence of a modulation of composition on the generation of defects in $In_{0.55}Ga_{0.45}As$ strained layers grown by MBE on InP substrates.

The most important feature that have been found in all the samples, is the existence of a tweed quasiperiodic structure with strong dark contrast roughly along both the [001] and [010] directions. The period Λ of this quasiperiodic structure has been found to be dependent on the layer thickness. It is worthwhile to point out that the interface dislocations network, expected in growth of mismatched layers, has not nucleated in any of the samples, even for the thicker one. Lattice parameter variations supose centres of localized strain avoiding dislocation to propagate and interact to form misfit segments generally in this structures. However, bidimensional defects are present with a density increasing with the thickness. The elastic energy associated with the modulation induced strain has been taken into account to expalin the found behaviour.

HIGHLY NON-LINEAR CHEMICAL RELAXATION IN STRAINED SEMICONDUCTORS

F. H. Baumann, A. Ourmazd, T. Y. Chang and J.- H. Huang
AT&T Bell Laboratories, Holmdel, N J 07733

Chemical relaxation of modern strained-layer heterostructures takes place under conditions which can otherwise be realized only in a diamond anvil. There is evidence that the initial stages of relaxation take novel pathways: ordering, phase separation and highly non-linear diffusion have often been ascribed to the enormous chemical gradients and stresses present in such systems. In metallic systems the presence of strain causes substantial changes in the formation and migration energies of native defects. In this paper we describe experiments designed to explore the initial chemical relaxation of highly strained semiconductors, and determine the effect of strain on the properties of the diffusing defects.

We use quantitative chemical mapping [1,2] to determine the interdiffusion of a series of $In_xAl_{1-x}As$ layers pseudomorphically grown on highly mismatched substrates. Our results show that as the composition of the diffusing layer changes from AlAs in tension to InAs in compression, the activation energy for diffusion changes from 4.8 to 0.6 eV. Since we directly measure the composition profiles of the individual diffusing layers, we are able to deduce separately the concentration-dependent and the concentration-independent enthalpies and entropies of the native defects involved in the diffusion process. These experiments allow us to explore the initial chemical relaxation of highly strained, highly non-linear systems in hitherto unexplored regimes. Most importantly, analysis of our results sheds light on the nonlinearities introduced separately by strain and composition.

REFERENCES

1. A. Ourmazd, D.W. Taylor, J. Cunningham, and C.W. Tu, Phys. Rev. Lett. **62**, 933 (1989).
2. A. Ourmazd, F. H. Baumann, M. Bode, and Y. Kim, Ultramicroscopy **34**, 237-255 (1990).

Session S

Surfaces and Low-D Structures

Friday, 26 July, 10:40 AM

Perella Auditorium

O SURROUNDING OF P_b DEFECTS AT THE (111)Si/SiO_2 INTERFACE

A. Stesmans
Department of Physics, Universiteit Leuven, 3001 Leuven, Belgium

The immediate oxygen surrounding in the silica side of the [111]P_b defect has been revealed for the first time from ^{17}O hyperfine (HF) structure electron spin resonance measurements at 4.3K on (111)Si/SiO_2 structures enriched to 51.24% ^{17}O. The [111]P_b defect, which is an $\cdot Si \equiv Si_3$ center with unpaired sp^3-like hybrid ⊥ interface, is the dominant defect generated at the (111)Si/SiO_2 interface as a result of lattice mismatch. Conventional as-oxidized (grown at ≈ 950°C in 1 atm dry O_2) (111)Si/SiO_2 structures typically comprise about 5×10^{12} P_b's cm^{-2} such that the P_b system constitutes a really 2-dimensional (2D) dilute spin system of spin S=½ (lattice site density in a (111)Si plane is 7.83×10^{14} cm^{-2}).

A key factor in the ^{17}O P_b HF structure identification is the correct evaluation of the dipolar interaction among P_b defects. These effects have recently been unveiled and exhibit the (structural) features characteristic for a 2D system as compared to the 3D case. This has allowed the separation of the dipolar effects and to tune their interference to a controlled amount by monitoring the P_b density using a reversible hyrogenation (passivation) technique. A comparison then of the P_b system of equal density grown in ^{17}O enriched and unenriched samples reveals the ^{17}O HF structure.

Analysing the structure along a simplified localized hybrid-atomic orbital picture shows that the sp^3 hybrid has its strongest HF interaction, characterised by the HF splitting constant $a_{\parallel 1}$=2.1±0.15 G, with only one O site in a first shell, a next interaction of $a_{\parallel 2}$=1.1 G with one O site in a second shell, and a third interaction of $a_{\parallel 3}$≈0.2 G with two equivalent O sites in a third shell. While these results complement the model of the P_b defect, the strenght of the ^{17}O HF interactions indicate, as expected, that oxygen is not incorporated in the central bonding structure of the P_b defect. In addition, the deduced "symmetry" of the O surrounding conflicts with an otherwise attractive previous model that pictures the immediate silica cap of a P_b defect as a puckered ditrigonal ring of six SiO_4 tetrahedra (generically referred to as the tridymite-like model). Rather, it is tentatively suggested from the present results that the immediate silica surrounding of the P_b consists of three fairly linearly arrayed SiO_4 tetrahedra.

If the P_b's are seen as somehow co-establishing the intrinsic Si/SiO_2 interface structure, this new insight may significantly contribute to uncover this structure.

Two-dimensionally Localized Vibrational Mode due to Al Atoms Substituting for Ga One-monolayer in GaAs

Haruhiko ONO and Toshio BABA

Fundamental Research Laboratories, NEC Corporation,
34 Miyukigaoka, Tsukuba, Ibaraki 305, JAPAN

It is well known that an impurity atom in a crystal has a localized vibrational mode (LVM) of TO-phonon, if the mass is lighter than that of host atoms. On the same principle, light impurities substituting for one-monolayer (1-ML) of host atoms may be expected to have a specific two-dimensionally localized vibrational mode (2D-LVM). In this paper, we demonstrate evidences of existence of such a phonon mode localized in 1-ML AlAs sandwiched by GaAs, by using infrared absorption spectroscopy. Furthermore, the observed phonon is shown to be a fundamental mode of two-dimensionally localized vibration causing the optical phonon confinement in AlAs/GaAs superlattices.

Samples used were grown on (001) GaAs substrates by molecular beam epitaxy. AlAs/GaAs superlattices or a single slab of 1-ML AlAs was sandwiched by GaAs. Infrared absorption spectra of the samples were observed by Fourier transform infrared spectroscopy at liquid He temperature.

A specific absorption peak was observed at 358 cm^{-1} with a line width of 3 cm^{-1} in a sample with 20 periods of $(AlAs)_1(GaAs)_{14}$ superlattice. Also in a sample with a single slab of 1-ML AlAs sandwiched by GaAs, completely the same peak was observed, except the peak height was 1/20; i.e., very strong confinement of TO-phonon was observed for the first time in the sample with a single slab of 1-ML AlAs. This 358 cm^{-1} peak is concluded to be the 2D-LVM due to two-dimensionally distributed Al atoms in three dimensional GaAs crystal.

Ab-initio Study of Boron delta-doped Silicon, M. SCHLUTER, M. NEEDELS, and M.S. HYBERTSEN, AT&T Bell Laboratories.- Because of the unique sub-surface position of the boron atom in the Si(111):B($\sqrt{3} \times \sqrt{3}$) surface, this structure has attracted considerable attention. Boron adsorbed on the technologically important Si(100) surface also forms an ordered reconstruction-(2x1). However, this system has hitherto attracted very little attention. We use first-principles total energy calculations to investigate the geometric and electronic structure of the Si(100):B(2x1) system. In particular, we discuss the energetics of B adsorbed at different sites on the Si(100) surface and the electronic structure of buried B delta-doped layers.

Scanning Tunneling Microscopy Studies of Semiconductor Surface Defects

J.E. Demuth
IBM Research Division
Thomas J. Watson Research Center
Yorktown Heights, NY 10598

Over the past years, there has been continued progress in characterizing and understanding a wide variety of point defects and metastable centers in bulk semiconductors. The recent application of Scanning Tunneling Microscopy (STM) to the study of semiconductor surfaces has revealed numerous defects and electrically active centers. The ability to directly probe local defects at semiconductor surfaces together with their local electronic and geometric structure may also prove useful in further understanding bulk defects and electrically active centers.

Here, various STM results of different semiconductor surface defects and their properties will be discussed. These include: anti-site defects in the Al/Si(111) surface, electron trapping centers on oxidized Si(111), the local structure of transition metal defects in Si as well as the detection of spin precession of individual "dangling bond" defects on Si(111).

POSTER SESSIONS

Session PA

Donors in Compound Semiconductors

Tuesday Evening, 23 July

Rathbone Hall

Laplace Transform DLTS Studies of the DX Centers in GaSb and AlGaAs

L. Dobaczewski,* I. D. Hawkins, M. Missous, I. Poole, and A. R. Peaker

Centre for Electronic Materials, University of Manchester Institute of Science and Technology, P.O.Box 88, Manchester M60 1QD, UK

The thermal emission of electrons from DX centers in III-V ternary semiconductors is associated with non-exponential transients. This has been attributed to the random alloy fluctuations. Recently, we found that the thermal emission process for the sulfur-related DX center in a binary, GaSb, is also strongly non-exponential. Detailed analysis of the process revealed that the DX centers form a negative-U system [1]. In the ground state the defect binds two electron, so the ionization process must go in two steps: $D^- \rightarrow D^0 + e^- \rightarrow D^+ + 2e^-$ and a two-component emission process is observed. For the DX centers in ternary compounds a simple deconvolution of the electron emission into two steps is not possible because the central atom of the defect has different local surroundings. The normal DLTS technique cannot resolve the multi-structure of the DX centers, because it has too low resolution and so it is not possible to distinguish between local alloy fluctuations and the two charge states of the center.

In the study we present for the first time the use of the Laplace transform for the analysis of multi-component emission transients observed from the DX centers. As a result it is possible to distinguish time constants with a resolution one order of magnitude better than the conventional DLTS technique. For the DX(S) in GaSb the Laplace-DLTS spectrum has two peaks. One of them is related to the ionization process of an intermediate D^0 thermodynamically unstable state of the DX defect. The other is the ionization process of the D^- ground state of the DX center. In contrast to the case of DX(S) in GaSb, the Laplace-DLTS spectra of the DX center in AlGaAs consist of series of very well-resolved peaks. More peaks can be observed when the DX defect is related to a group VI donor element (tellurium) than for a group IV (silicon). This is because when the donor substitutes the As-atom in AlGaAs it can have more local configurations than when it occupies Ga or Al sublattice. Laplace-DLTS spectra taken for different filling pulses clearly show that some of the peaks can be related to the emission process from the thermodynamically unstable D^0 states of DX in different local alloy configurations. Moreover, the Laplace-DLTS spectra taken at different electric fields show that for some of the peaks a Poole-Frenkel effect can be observed allowing the observed emission processes to be related to different charge states of the DX defect.

Laplace-DLTS technique gives a direct insight into the local environment surrounding the DX defect, allowing the charge state of the defect in each of the local alloy configuration to be investigated, as well the electron capture process for each of the configuration.

* Permanent address: Institute of Physics, Polish Academy of Sciences, Warsaw, Poland.

1. L. Dobaczewski, P. Kaczor, J. M. Langer, A. R. Peaker, and I. Poole, *Proceedings of 20ICPS, Thessaloniki*, to be published.

A photoluminescence study of the charge states of a donor level in GaAs induced by hydrostatic pressure

X. Liu, L. Samuelson, M.-E. Pistol
Department of Solid State Physics, University of Lund,
Box 118, S-221 00 Lund, Sweden

Although the negative-U model for the DX centre[1] is still controversial, most experiments have either supported the model or been inconclusive. Nevertheless, no one has used the photoluminescence (PL) spectroscopy to test the validity of the model. If a donor state involved in a DA recombination is a negative-U centre binding two electrons, we would predict the Coulomb term in the DA recombination energy is zero in both initial and final states. The DA peak in a PL spectrum is then expected to show no red shift with time decay, no blue shift with increasing excitation density, since there is no difference in recombination energy for a closer or more distant pair.

A novel donor state (D^*) induced in the band gap of GaAs by hydrostatic pressure was observed as a donor-acceptor (DA) peak D^*A in PL spectra[2]. Based on (i) its omnipresence in different samples, (ii) the critical pressure it appears, (iii) the energy position estimated at atmospheric pressure, (iv) the comparison with PL in alloys, and (v) the D^*A pressure coefficient, we suggest that D^* be related to the DX centres observed in GaAs and some alloys. However, it exhibits in the PL spectrum only a small lattice relaxation and no photoquenching is observed in the time scale of seconds to minutes. Our PL investigation of the D^* state yield results implying its positive-U property. The D^*A peak does show a weak red shift with time decay, and a blue shift with increasing excitation. Moreover, a shifting peak M observed on the high energy side of D^*A peak when the excitation photon energy is below band gap is attributed to the closer D^*A pairs. This peak M is concluded to be due to the resonant excitation of an electron on the D^* donor state with the creation of an excited hole on the adjacent acceptor. This excitation is followed by the relaxation of the electron-hole pair, resulting in the M luminescence peak. The change of the M peak energy with the energy of the exciting laser is due to the excitation of pairs of different separations arising from the Coulomb term, also implying a positive-U property of the D^* state. The existence of such a D^* state may be consistent with the negative-U model for the DX centre if D^* is the unrelaxed neutral donor state binding one electron.

1). D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **61**, 873 (1988), & Phys. Rev. B **39**, 10063 (1989).
2). X. Liu, L. Samuelson, M.-E. Pistol, M. Gerling, and S. Nilsson, Phys. Rev. B **42**, 11791 (1990).

DX Centers in MOCVD-Grown Si-Doped $Al_xGa_{1-x}As$ Containing Boron

P.M. Mooney, M.A. Tischler, and B.D. Parker
IBM Research Division, T.J. Watson Research Center
PO Box 218, Yorktown Heights, NY 10958 USA

DX centers in $Al_xGa_{1-x}As$ are now understood to be ground states of substitutional donors in distorted configurations. The substitution of Al or In for Ga has been shown to alter the thermal emission rates of electrons from DX centers in Si-doped material. Recently it was reported that the DLTS peak of the DX center typically observed in Si-doped GaAs under hydrostatic pressure was not observed in LEC-grown Si-doped GaAs samples contaminated with boron. This indicates that the presence of small concentrations of boron modifies the properties of Si donors. Since the presence of DX levels makes n-type $Al_xGa_{1-x}As$ unsuitable for some interesting technological applications, we have investigated the effects of boron on the properties of silicon donors in epitaxial AlGaAs layers grown by MOCVD.

A series of Si-doped AlGaAs layers having different concentrations of boron, up to $6x10^{18}$ cm^{-3}, was grown for our experiments. The electrical characteristics of these layers were studied using C-V, Hall effect, and DLTS measurements. The reduction in free electron concentration compared to the donor concentration in the boron-doped samples is roughly comparable to that in samples of the same alloy composition without boron. The concentration of free electrons after photoexcitation at 80K, however, decreases with increasing boron concentration. The DLTS peak characteristic of DX centers was observed in all our samples; however, consistent with the decreasing PPC, the occupation of the DX levels also decreases with increasing boron concentration. Unlike for boron-doped GaAs under pressure, no other deep levels in large concentration were observed by DLTS in these samples.

We infer from these measurements the presence of another deep level, lying below mid-gap in energy, with at most only a small barrier to electron capture. The concentration of this level increases with increasing boron concentration and must be comparable to the Si donor concentration in the samples having the highest boron concentration. The data suggest that this deep level is associated either with boron or with a contaminant which is incorporated into the lattice along with the boron. The boron concentrations both in these samples and in the boron-doped GaAs samples of the earlier experiments are very low compared to the concentrations of Al or In required to modify the characteristics of the DX centers. This indicates that the role of boron (or other contaminant) is quite different from that of Al or In in this material. Possible mechanisms to explain our results will be discussed. We conclude that, due to the presence of this deep level, n-type AlGaAs with boron added, like n-type AlGaAs without boron, is unsuitable for some device applications.

DISCOVERY OF A NEW METASTABLE STATE OF THE DX CENTER IN Si DOPED $Al_{0.26}Ga_{0.74}As$.

Pavel BRUNKOV, Aleksey KOMMISSAROV, Vadim EVTIKHIEV, Samuel KONNIKOV, Mikhail SOBOLEV.
A.F.Ioffe Physical Technical Institute, Acd.Sci.USSR, Polytechnicheskaya 26, 194021, Leningrad, K-21, USSR

We have studied DX-center in MBE-grown Si-doped ($n \sim 1\times10^{17}cm^{-3}$) $Al_{0.26}Ga_{0.74}As$ layers both GaAs/AlGaAs heterostructure single quantum well lasers and Au-$Al_{0.24}Ga_{0.76}As$ Schottki diodes using DLTS, TSCAP, fotoconductivity as well as modulation methods.

Measurements of TSCAP spectra showed that two deep levels with thermal activation energy E_1=442 meV and E_1^*=181 meV were presented in Si-doped $Al_{0.24}Ga_{0.76}As$ layers. The first level has been identified as DX-center by means of DLTS measurements. The second level has not been observed in DLTS spectra. Appearence of these E_1 and E_1^*levels in TSCAP spectra depended upon the cooling conditions of the sample to the initial measurements temperature (~80 K). The level E_1 disappeared when sample was cooled under revers bias $U_o < 0$ and the level E_1^*-zero bias $U_o = 0$. The performed isochronal annealing of the sample have shown the presence of the temperature threshold $T_{th} \sim 150$ K corresponding to a reversible transition from one TSCAP spectrum with level E_1 to another one with level E_1^*. The sum of the first and the second step heights of TSCAP curves corresponding to E_1 and to E_1^* levels was constant at all annealing conditions. Thus, there are two state of DX-center The thermal activation energy of the transformation from the stable state to metastable one and vice verse were defined. They were corresponded to E_e=367 meV and to E_b=128 meV. It was concluded that the stable state of DX-center is characterized by the self-trapped level and the metastable one - the "ordinary" level.

ODEPR OF THE DEEP PARAMAGNETIC STATE OF IONIZED DX CENTERS IN Sn AND Si DOPED $Al_xGa_{1-x}As$

M. Fockele+, J.-M. Spaeth+, P.Gibart++ and H. Overhof+

+ University of Paderborn, Fachbereich Physik, Warburger Str. 100 A, D-4790 Paderborn, F.R.G.
+ + Laboratoire de Physique du Solide et Énergie Solaire, CNRS, Sophia Antipolis, 06560 Valbonne, France

DX centres were investigated in Sn and Si doped $Al_xGa_{1-x}As$ layers with the magnetic circular dichroism of the absorption (MCDA), optically detected EPR (ODEPR) and photoconductivity (PC). Upon photoionization of the DX centers at 1.5K with a threshold of 0.9eV an IR-MCDA band appears between 0.73 and 1.5eV correlated with the appearence of the PC. The MCDA-detected ODEPR spectrum due to Sn^0 ($S=1/2$, $g=1.97 \pm 0.03$) shows hyperfine (*hf*) doublets from ^{117}Sn and ^{119}Sn ($I=1/2$ with an isotropic *hf* constant of 10.1GHz (^{117}Sn) [1,2]. Comparison with conventional EPR shows that both methods show the same spectrum [3,4] and that the number of Sn^0 atoms is approximately that of the dopants. At 1.5K both the PC and MCDA signals decrease thermally according to the same function. The decrease can be accelerated by illumination with light below 0.75eV. After the decay DX is formed in its ground state and can be photoionized once more. The observation of the MCDA band and of the *hf* interaction which is equivalent to a spin localization at Sn^0 of about 13% implies that Sn^0 is a deep center. From ODEPR detected in the IR luminescence at 1.5 μm the same *hf* split Sn^0 spectrum is measured superimposed on the spectrum of an As antisite defect, which acts as a shunt center for the emission and can also be seen in MCDA-detected EPR at 0.95 μm. In Si-doped layers with the MCDA and the emission technique the same Si^0-related ODEPR spectra were measured ($g= 1.95 \pm 0.03$, $\Delta B_{1/2}=8mT$), the latter again via an As_{Ga} antisite defect. We conclude that the DX ground state must be negatively charged with negative U properties and that the singly ionized state DX^0 is a deep state which probably has also a large lattice relaxation configuration.It has a thermal barrier against capturing an electron to form DX^-. The IR emission at 1.5 μm assoziated with the DX center is not related to the dopant.

1) M. Fockele, J.-M. Spaeth and P. Gibart, Mat. Sci. For. 65-66, 443, 1990
2) M. Fockele, J.-M. Spaeth and P. Gibart, Proc. 20th ICPS 1990, World Scientific, Vol 1, 517
3) H. J. von Bardeleben, J.C. Bourgoin, P. Basmaji and P. Gibart, Phys. Rev. B40, 5892, 1990
4) H. J. von Bardeleben, private comunication

LIMITATIONS OF ION CHANNELING FOR THE STUDY OF BISTABLE DEFECTS

Thomas N. THEIS, Alan D. MARWICK and Benjamin D. PARKER
IBM Research Division, T.J. Watson Research Center, Yorktown Heights, NY USA 10598

Although the model of the DX center proposed by Chadi and Chang is becoming widely accepted, several experimental results in the literature are still in apparent contradiction to the model. One example is a recent ion-channeling experiment of Yu *et al.*[1] which is interpreted to indicate that Sn donors in $Al_xGa_{1-x}As$ remain on a substitutional site upon electron capture to the DX state. This interpretation contradicts not just the model of Chadi and Chang, but also alloy perturbation experiments which show clearly that the substitutional symmetry of the column IV donor is broken in the DX state.

Yu *et al.* assumed that ion-beam damage to the upper 2.5 μm of their sample was negligible, but did not make any measurements to verify this assumption. We have continuously measured the electrical resistance of a 2 μm thick heavily Sn-doped $Al_xGa_{1-x}As$ surface layer during an equivalent ion-beam exposure. For fluences up to 5×10^{14} cm^{-2}, the sample resistance increases exponentially with dose. Apparently the energetic ions generate many defects (with associated gap states) in the upper 2 μm of the sample. Our analysis indicates that the minimum ion fluence used by Yu *et al.* to obtain an ion-channeling spectrum would have generated enough gap states to greatly reduce the occupation of the DX state. Under this condition, nearly all donors would be expected to occupy substitutional sites, consistent with the reported data.

Our results put constraints on the use of ion-channeling techniques for the study of DX centers and other bistable defects. We conclude that the published ion-channeling results neither confirm nor contradict the model of Chadi and Chang. We also examine the published extended x-ray absorption fine structure (EXAFS) studies of the DX center, and come to a similar conclusion.

1. K.M. Yu, K. Khachaturyan, E.R. Weber, H.P. Lee, and E.G. Colas, Phys. Rev. B43, 2462 (1991).

STUDIES OF DEEP LEVEL TRANSIENT SPECTROSCOPY OF DX CENTERS IN GaAlAs:Te UNDER UNIAXIAL STRESS

Ming-fu Li [1,2], Peter Y. Yu[1,3], E.R.Weber [2,3], E. Bauser[4]
W. L. Hansen[3], and E. E. Haller[2,3]

[1]Department of Physics, University of California, Berkeley, CA 94720
[2]Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA 94720
[3]Materials Science Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720.
[4]Max-Planck-Institut für Festkörperforschung, D-7000,Stuttgart 80, Germany.

DX centers in $Al_{0.38}Ga_{0.62}As$:Te have been studied by Deep Level Transient Spectroscopy (DLTS) as a function of uniaxial stress along the [100], [110] and [111] directions. No splitting nor broading of the DLTS peaks was observed for stress up to 10 kbar. Instead the peaks shift very nonlinearly with stress in ways strongly dependent on the stress directions. Our results have been analyzed both in terms of small lattice relaxation and large lattice relaxation models. Our results cannot be explained satisfactorily by small lattice relaxation models in which the DX center follows the L conduction valleys as a function of stress. Numerical simulations of DLTS spectra based on large lattice relaxation models of the DX center are found to explain the experimental results qualitatively. One feature of the large relaxation model which is crucial to the success of this explanation is that the lattice relaxation occurs in a time scale comparable or shorter than the capture time.

Session PB

Wide Band-Gap Semiconductors

Tuesday Evening, 23 July

Rathbone Hall

ACCEPTORS IN SILICON CARBIDE: ODMR DATA

Pavel G.BARANOV and Nikolai G.ROMANOV
A.F.Ioffe Physico-Technical Institute, Acad.of Sciences of USSR,
194021 Leningrad, USSR

Optically detected magnetic resonance (ODMR) has been used for a study of acceptors in bulk crystals and epitaxial layers of 4H and 6H polytypes of SiC doped with B, Ga, Al, and Sc. ODMR of donors and acceptors was recorded by monitoring the intensity of photoluminescence. Selective excitation of emission allowed to distinguish between the epilayer and the substrate. Nitrogen was identified as a donor by observing the resolved hyperfine (hf) interaction with the ^{14}N nucleus. ODMR spectra of acceptors were characteristic of the impurity and showed a decrease of the anisotropy in the row Al, Ga, Sc, B.

Strongly anisotropic ODMR of acceptors was recorded in Al and Ga doped SiC [1,2]. A resolved hf interaction with the Ga nucleus was the first observation of hf structure for the effective-mass-like acceptors. This gave the direct measure of the unpaired electron spin density at the Ga nuclei in cubic and hexagonal lattice sites and allowed to estimate the localization of Al and Ga acceptors.

A number of anisotropic signals ascribed to acceptors were found on the "yellow" luminescence in boron doped 6H-SiC. Although the configuration of the valence electron shell of boron is similar to that of aluminium and gallium, the ODMR spectra in SiC:B were considerably different. This difference could be explained if we suppose that B occupies the carbon site in the lattice whereas Al and Ga substitute silicon. It is also possible that the boron-vacancy complex is involved in the recombination process.

A very complex ODMR spectrum was found in 4H- and 6H-SiC doped with Sc. The spectrum consists of the isotropic donor signal and a number of anisotropic lines. Two groups of lines can be distinguished: Sc(1) ($S=1/2$, $g_{//} = 1{,}97$ and $g_{\perp} = 2{,}49$) and Sc(2) ($S=1/2$, $g_{//} = 1{,}21$; $1{,}18$; $1{,}17$ and $g_{\perp} = 1{,}77$; $1{,}63$; $1{,}41$ respectively). They seem to be connected with different charge states of Sc. Sc(1) and Sc(2) spectra consist of several overlapping lines which apparently belong to different lattice sites. A neutral acceptor A^{o} may be a model of Sc(1). Sc(2) seems to be a doubly charged acceptor A^{2-}(3d). Due to the interaction of the d-electron of Sc with the valence band of SiC quasi d-states of the acceptor in the band gap may exist. This can explain the different anisotropy of Sc acceptors as compared to Al and Ga.

By observing double and triple quanta resonances in the ODMR spectra we discovered that the Zeeman levels of Sc(1) were not linear. Such a non-linearity seems to be connected with an influence of other closely lying energy levels. The energy separation between these levels is estimated. In ODMR of N, Al, Ga and B in 4H and 6H SiC no non-linearity effects were found.

A large hf splitting (26 mT, I=1/2) was observed in ODMR of some SiC crystals grown with the excess of carbon vacancies. One can not exclude that the spectrum is related to an antisite defect.

1. Le Si Dang, K.M.Lee, G.Watkins, and W.J.Choyke, Phys.Rev.Lett. 45, 390-394 (1980).
2. P.G.Baranov, N.G.Romanov, V.A.Vetrov and V.G.Oding in: The Physics of Semiconductors (Proc.20th Int. Conf., Thessaloniki 1990), v.3, p.1855-1858, World Scientific 1990.

INFRARED ABSORPTION AND LUMINESCENCE OF VANADIUM (V^{4+}) IN SILICON CARBIDE

A. Dörnen, W. Suttrop * and G. Pensl *
4. Physikalisches Institut, Universität Stuttgart, F.R.G.
* Institut fur Angewandte Physik, Universität Erlangen, F.R.G.

We present optical absorption and luminescence measurements on the internal transitions of V^{4+} ($3d^1$) in silicon carbide. The identification of these lines was shown previously in a work combining both, optical methods and EPR measurements [1]. The lines were related to transitions between $T_2(3d^1)$ and $E(3d^1)$ states [1].

We find a characteristic persistent optical activation of the V^{4+} absorption lines in p-type samples. In n-type material no activation is necessary to observe these lines. The persistent activation in p-type material is due to a permanent transition from the 5+ to the 4+ charge state by an electron capture process. Once activated, the 4+ charge state is stable up to temperatures of about 100 K. From the spectral dependence of this activation, we find the 5+/4+ transition of vanadium in the 6H- polytype material to be a midgap level, located about 1.5 eV above the valence band.

Zeeman measurements on the internal transitions of V^{4+} are presented and compared with g-factor values obtained in EPR measurements [1]. We find the upper ground state - not observed in EPR - to show a zeeman splitting which is different from the predictions drawn from by crystal-field theory. Consequences for the level scheme will be discussed.

In p-type 6H material with high aluminum concentration, another set of lines additionally to the above mentioned system is observed in luminescence and absorption. The overall characteristics of this spectrum $V^{4+}(X)$, including the activation process, are very similar to the V^{4+}-lines. We conclude that the $V^{4+}(X)$ center is basicly vanadium modified by a different impurity, probably aluminum on a nearest neighbour site.

[1] J.Schneider, H.-D.Müller, K.Maier, W. Wilkening, F.Fuchs, A. Dörnen S.Leibenzeder, and R.Stein, Appl. Phys. Lett. 56, 1184 (1990)

LUMINESCENCE OF A 4d-CENTRE IN ZnS

R.Heitz, P.Thurian, A.Hoffmann and I.Broser
Institut für Festkörperphysik
Technische Universität Berlin, Germany

Recently, a structured luminescence band in the near infrared spectral region has been reported for ZnS [1]. The extraordinary high number of phonon satelites of over 70 lines was explained by local vibrations of a complex formed by two sulphur vacancies, a so called M-centre [2]. In the present paper we report new experimental results indicating the luminescent centre being an isolated impurity. Possible candidates are substitutional 4d-ions with a d^4-configuration. This is the first structured luminescence of a 4d-element in a II-VI semiconductor and offers insight in the interesting physical properties of such a centre.
Careful performed spectroscopic measurements of the zero phonon region around 1.513eV reveal a rich pattern of lines strongly depending on the structure of the investigated crystal. It is shown that all lines belong to different polytypic centres, whereby the cubic transition is symmetry forbidden and therefore very weak. Zeeman measurements reveal a singlet ground state and a triplet excited state. Since all observed lines exhibit the same Zeeman behaviour the ground state has to be an electronical singlet, given by a d^4-configuration in the low spin case. This can explain also the excitation spectrum which show additional intra centre transitions around 1.7eV and 2.33eV.
Possible candidates for the luminescent centre are Nb^{+} and Mo^{2+}. The strong crystal field induced by the large size mismatch with the substituted Zn-ion leads to the low spin configuration. The large mass difference of about 50% results in distinct local vibrations at the impurity centre explaining the rich sharp phonon spectrum. The importance of the phonon coupling is also demonstrated by temperature dependent measurements. With rising temperature a second dipol allowed zero phonon line appears displayed by 3.33meV to higher energies. Their Lorenzian profil with an half width of 1.2meV indicates a very fast relaxation in the femtosecond regime. The energy splitting of the excited state correspond very well to a frequent distance in the phonon wing of 3.17eV.

[1] I.Broser, R.Germer, F.Seliger and H.J.Schulz, J.Phys.Chem.41 (1980), 101

[2] R.Germer, Phys.Rev.B27 (1983),2412

THEORY OF NITROGEN AND PLATELETS IN DIAMOND.

P. R. BRIDDON, M. I. HEGGIE and R. JONES
Department of Physics , University of Exeter , EX44QL, UK

ab initio calculations are carried out on an isolated N impurity and aggregates of N in diamond. We find the substitutional impurity has C_{3v} symmetry with both N and one of the neighbouring C atoms being displaced outwards by $\approx .2$ Å. The other C atoms move towards the N atom. Two E vibrational modes are found: one at 1332 cm^{-1} due to C-C vibrations and a broad band around 1080 cm^{-1} due to N-C vibrations. These account for the observed N-related modes at 1344 and around 1130 cm^{-1} respectively
The calculated normal coordinates explain why the first is insensitive to doping with N isotopes. Two A_1 electronic levels are found in the gap accounting for the several absorption edges that are observed.
We have also investigated the Lang model of the platelet and find it is unable to explain either the B′ band at 1372 cm^{-1} or the luminescence at 1.25 eV. On the other hand, we find the N-C platelet model of Humble does account for these observations as well as the low frequency 326 cm^{-1} platelet band. A simple model is given for the aggregation process leading to this model of the platelet.

INTERSTITIAL DEFECTS IN II-VI SEMICONDUCTORS: ROLE OF THE CATION *d* STATES[1]

J. T. SCHICK,[2] C. G. MORGAN-POND, and J. I. LANDMAN
Department of Physics and Astronomy, Wayne State University, Detroit, MI 48202, USA

Since point defects, including interstitials, play a major role in determining the electronic properties of II-VI semiconductors, a full understanding of these properties requires an accurate description of the important point defects in these materials. With the exception of some recent work which considers tetrahedral interstitials and some non-interstitial defects in ZnSe[3], most calculations of interstitial properties in II-VI semiconductors neglect the effects of the cation *d* states on the bonding, though calculations of bulk properties have shown[4] that these effects are often important in II-VI semiconductors containing Zn, Cd, or Hg. Although some point defects, such as antisite and substitutional impurity defects, alter only the atomic species occupying one lattice site, interstitial defects involve local atomic coordination which is incompatible with tetrahedral sp^3 bonding. The *d* states may therefore play a significant role in determining interstitial properties, particularly for interstitial sites with lower than tetrahedral symmetry.

Calculations of the localized electronic defect states due to tetrahedral and hexagonal interstitials in CdTe and ZnTe have been carried out both with and without *d* states included in the valence band basis set. Both cation and anion interstitials are considered. We have used a tight-binding Hamiltonian with a basis of realistic (Hartree-Fock) atomic orbitals,[5] including non-zero overlap. Charge transfer is treated self-consistently. A supercell size of 65 atoms has been found to be sufficient for an accurate characterization of the properties of an isolated defect. Similar calculations have been carried out for vacancies in these materials, for the purposes of comparison.

We discuss the effect of the *d* states on the energy levels and electron densities associated with the localized defect states of these interstitials and vacancies, and examine the importance of the magnitude of the deviation from ideal tetrahedral coordination in determining the role of the *d* states in the formation of the defect states.

[1] This work was supported in part by the Night Vision and Electro-Optics Laboratories and the ARO under ARO Grant No. DAAL03-87-0061, and by the Institute for Manufacturing Research.
[2] Present and permanent address: Department of Physics, Villanova University, Villanova, PA 19085, USA.
[3] D. B. Laks et al., Phys. Rev. Lett. 66, 648 (1991).
[4] S.-H. Wei and A. Zunger, Phys. Rev. B 37, 8958 (1988).
[5] E. Clementi and C. Roetti, At. Dat. Nucl. Dat. Tables 14, 177 (1974).

The Structure of the D-Center in Silicon Carbide -A Study with Electron Nuclear Double Resonance

S. Greulich-Weber, R. Müller and J.-M. Spaeth

University of Paderborn, FB6 - Experimentalphysik, Warburger Str. 100A, 4790 Paderborn, FRG

S. Leibenzeder and R.A. Stein

Siemens AG, Paul-Gossen-Str. 100, 8520 Erlangen, FRG

Boron-doped 6H-SiC has been studied for many years intensively . With DLTS the isolated boron acceptor and a deep donor called D-center were observed ([1],[2]). The D-center was assumed to be a boron-vacancy complex. Up to now neither the structure nor the chemical composition of the D-center is known. In order to determine the electronic and microscopic structure of this defect we investigated boron doped 6H-SiC with Electron Nuclear Double Resonance (ENDOR). To correlate our ENDOR measurements with the energy levels known from DLTS for boron-related defects Photo-EPR (Electron Paramagnetic Resonance) and Photo-ENDOR measurements were carried out. From those measurements it is clear that with ENDOR indeed the D-center was investigated. Our ENDOR measurements show that boron is a component of the D-center. From symmetry and quadrupole interactions observed we conclude that the D-center is not an isolated boron defect, but perturbed by an adjacent defect. The microscopic structure of the D-center as determined from our ENDOR analysis will be discussed.

[1] W. Suttrop, G. Pensl, P. Lanig, Appl. Phys. A51, 231-237 (1990)
[2] G. Pensl, R. Helbig, Advances in Solid State Physics, Vol 30 (1990)

FERROELECTRIC PHASE TRANSITIONS INDUCED BY OFF-CENTER IMPURITIES IN NARROW GAP IY - YI SEMICONDUCTORS

Boris Vugmeister
Physics Department, Building 16, Lehigh University, Bethlehem, PA 18015, USA

The review of experimental and theoretical investigations of the effect of off-central impurities Ge^{2+} , S^{2-} on the structure instability of narrow gap mixed semiconductors $Pb_{1-x}Ge_x Te$, $Pb\,Te_{1-y}S_y$ is given.
The nature of the phenomena is connected with the peculiarities of dipole-dipole interation potential between off-center ions in highly polarizable crystals PbTe comparing with those in ordinary dielectrics of NaCl type[1]
The phase diagram of such compound including the region of concentrational ferroelectric phase transition can be explained self-consistently by the random local field approximation[2], which in contrary with the mean field theory takes into account the distribution of the local field acting on every off-center ion from its neighbours.The thermodynamic parameters such as critical concentration , ferroelectric transition temperature, specific heat, dielectric permitivity, as well as electrical resistance $\rho(T)$ are calculated. The anomalous increasing of $\rho(T)$ at low temperature (Kondo-like effect) we could explain taking into account the effect of spatial disorder in orientations of the off-center ions at low temperature.
The phase diagram in fourfold solutions of $Pb_{1-x}Te_{1-y}Ge_x S_y$ type is analyzed and shown that due to nonequivalency of the different positions of off-center ions it is necessary to take into account the existence of additional static random field which complicates phase diagram.The attempt is made to estimate the impurity off-central displacement.We discuss also different mechanisms leading to the appearance of off-central ions in narrow gap semiconductors.

1. B.E.Vugmeister, M.D.Glinchuk. Rev.Mod.Phys. 62, 993,1990.
2. B.E.Vugmeister, V.V.Stefanovich. Solid State Commun. 67, 323,1987.

PAC Study of the Acceptor Li in II-VI Semiconductors

H. Wolf, Th. Krings, Th. Wichert

Technische Physik, Universität des Saarlandes, 6600 Saarbrücken, FRG

Detailed information on the atomic configuration of dopant atoms is much less available for II-VI semiconductors than for elemental or III-V semiconductors. But, in II-VI semiconductors doping, in particular p-doping, poses a crucial problem because of the strong interaction of the dopant atoms with intrinsic defects leading to self-compensation phenomena. Since Li, introduced on the group-II site, is regarded as a promising candidate for p-doping of II-VI semiconductors we have begun investigating its incorporation in the II-VI lattice on an atomic scale. For this purpose, the donor ^{111}In is introduced as a probe atom in order to look for the Coulomb-driven formation of the donor-acceptor complex In_{II}^{+}-Li_{II}^{-}. Such a pairing is easily detectable by the perturbed angular correlation technique (PAC) via the Li specific electric field gradient [1].
It has been shown that diffusion of CdS with ^{111}In under excess S leads to the formation of In_{Cd}^{+}-V_{Cd}^{-} pairs, where V_{Cd}^{-} is the acceptor-like Cd vacancy; under excess Cd these pairs vanish and isolated In_{Cd} is left behind [2]. We have diffused CdS:^{111}In crystals with Li at 800 K in an evacuated quartz ampoule for 30 minutes. After this procedure no In_{Cd}^{+}-Li_{Cd}^{-} pairs were detectable but a high fraction of the In_{Cd}-V_{Cd} pairs. During annealing of CdS these pairs vanish at a significantly lower temperature than those produced by firing under excess S. Additional experiments indicate that this lower thermal stability can be related to the outdiffusion of Li atoms. From these observations we conclude that Li does not resides in the Cd sublattice as an acceptor [3] but rather goes interstitially as a donor thereby creating a V_{Cd} defect. That means, in CdS the donor In and the acceptor Li both are compensated by the action of the V_{Cd} defect. The results will be compared with PAC results obtained for other II-VI semiconductors, like ZnO [4] and CdTe [5], and the implications for the possibility of p-doping using Li as a donor will be discussed.

1) Th. Wichert, this conference.

2) R. Magerle, M. Deicher, U. Desnica, R. Keller, W. Pfeiffer, F. Pleiter, H. Skudlik, and Th. Wichert, in: E-MRS 1990 Fall Meeting, Symposium D, in print.

3) R.N. Bhargava, J. Cryst. Growth 59 (1982) 15.

4) H. Wolf, S. Deubler, D. Forkel, H. Foettinger, M. Iwatschenko-Borho, F. Meyer, R. Renn, W. Witthuhn, and R. Helbig, Materials Science Forum 12 (1986) 863.

5) D. Wegner and E.A. Meyer, J. Phys.: Condensed Matter 1 (1989) 5403.

THE ROLE OF VACANCIES IN STABILIZING THE GROWTH OF DIAMOND AND CUBIC BN

T. LEI, Y. BAR-YAM, and T.D. MOUSTAKAS
ECS, 44 Cummington St., Boston University, Boston, MA, 02215

Vacancies have recently been proposed to play a crucial role in stabilizing the nucleation and growth of diamond on non-diamond substrates.[1,2] By introducing non-equilibrium vacancies during growth in both diamond and graphite the relative binding energy of the two materials is changed and the free energy of diamond is lower. In a quasi-thermodynamic picture diamond nucleates and grows under these conditions. Experimental results which detect large point defect concentrations support this picture. Moreover, because the defect formation energy depends on the Fermi energy, a dramatic increase in nucleation and growth with Fermi energy shifts is predicted and has been observed. Similarly to diamond, cubic boron nitride is thermodynamically unstable to hexagonal boron nitride. In boron nitride, vacancies can be introduced in a controlled way by off-stoichiometry. Ab-initio calculations of the formation energies of boron and nitrogen vacancies in cubic and hexagonal boron nitride can thus be directly compared with experimental results on the stoichiometry dependent growth of cubic boron nitride and hexagonal boron nitride. Indeed, the successful growth of cubic boron nitride implies that defects and defect dynamics plays an important role in this growth.

[1] Y. Bar-Yam and T.D. Moustakas, Nature 342, 786 (1989)
[2] Y. Bar-Yam and T.D. Moustakas, Mater. Res. Soc. Symp. Proc. 162, 201 (1989)

Session PC

Theory

Tuesday Evening, 23 July

Rathbone Hall

DONOR BISTABILITY INDUCED BY ELECTRON-PHONON COUPLING

S. BEDNAREK and J. ADAMOWSKI
Institute of Physics and Nuclear Techniques, Academy of Mining and Metallurgy, PL-30059 Kraków, Poland

We propose a microscopic theoretical model for bistable donors in polar crystals. This model allows to explain the experimental results for the donors in the cadmium fluoride crystals. The present approach is going beyond the effective mass approximation. Instead, the one-band approximation is used in which the finite width and non-parabolicity of the conduction band are included. The actual shape of the conduction band is proposed in an analytical form which is consistent with the experimental data for the optical absorption. Taking into account the polar coupling of the donor center and the electron to the phonons, we obtain the coexistence of the strongly and weakly localized donor states. For the isocoric indium donor, for which the short-range donor potential can be neglected, the calculated energy for the strongly localized state is lower than that for the weakly localized state and the donor exhibits the bistability properties. However, for such donors as Y, Gd, Yb, the short-range potential shifts the energy of the strongly localized state upwards. Thus, these defects introduce into the band gap the shallow energy levels only, and are stable. The calculated energy levels for all the donor states are in good agreement with experiment. Moreover, the present approach explains the other effects observed in the optical absorption on the stable and bistable donors. First, the absorption band shape for the bistable donors in the 3-eV region is correctly reproduced. Second, the difference in the infrared absorption between both the types of donors can be explained. This absorption is due to the transitions between the shallow donor states and the conduction band and is the characteristic property of the stable (Y) and bistable (In) donors. The absorption band maxima are shifted with respect to each other by 75 meV, although the relative shift of the 1s-2p transitions is merely 5 meV. The shape of both the absorption bands is also different, i.e., this for Y is much narrower than that for In. We show that these properties result from the different localization of the electron bound to both the donors.

Theoretical Study on the Structure and Properties of Dislocations in Semiconductors

K. Masuda-Jindo

Department of Materials Science and Engineering,
Tokyo Institute of Technology
Nagatsuta, Midori-ku, Yokohama 227, Japan

We investigate atomic configurations and electronic states of dislocations in covalent semiconductors using LCAO (linear combination of atomic arbitals) recursion electronic theory [1,2]. Particular attention will be focused on the determination of band gap states associated with the straight dislocation line and point like singularities ("solitons" and segregated impurities) in the dislocation core region. This type of calculation is of great significance since the gap states play an important role in determining the electrical and dynamical properties of dislocations [3,4]. For the electronic structure calculation of dislocations, we use LCAO recursion method and termination procedure based on the perturbation theory [2], to remove the spurious structures in the local density of states. The calculated electronic states of dislocations are compared with previous calculations as well as the available experimental results [4].

The following points are discussed in detail.

(1) Both for 90° partial and 30° partial dislocations, the energy differences between reconstructed and unreconstructed configurations are calculated.

(2) The energy levels associated with the reconstruction defects ("solitons") are calculated and compared with those of the straight reconstructed dislocation core.

(3) Using the calculated electronic structure of the dislocation, we discuss the doping dependence (electrically active impurities) of dislocation motion as well as the recombination enhanced dislocation motion.

It has been shown that core reconstruction influences quite significantly the electronic states of the dislocations: Interestingly enough, we have found that the isolated "soliton" in the dislocation core can produce prominent deep levels in the band gap, even for the reconstructed core with small atomic displacements. (This is consistent with the recent experimetal observation using the high resolution electron microscopy that there is no strong evidence for core reconstruction of 90° partial dislocation in Si crystal [5].)

[1] K. Masuda-Jindo, Int. Conf. on "The Science and Technology of Defect Control in Semiconductors", 1989, Yokohama P.85.
[2] K. Masuda-Jindo, Phys. Rev., B41, (1990) 8407.
[3] Y. Fujita and K. Masuda-Jindo, J. Appl. Phys. 67, (1990) 2965; ibid, (1991) April issue, in press.
[4] N. Maeda and S. Takeuchi, Proc. 6th Int. Symp. on the Structure and Properties of Dislocations, Oxford, 1989.
[5] S. Takeuchi, private communication.

THE TEMPERATURE DEPENDENCE OF TRAP CROSS SECTIONS

J. P. LAVINE, E. K. BANGHART, E. T. NELSON, W. DesJARDIN, and B. C. BURKEY
Image Acquisition Products Division, Eastman Kodak Company, Rochester, NY 14650-2008, USA

Many trap cross sections vary with temperature T. A power law is usually used to carry the cross section far from established data, but existing theories provide a range of power laws. Experimental data are lacking above 25 K for important traps such as phosphorus in silicon. Charge packet transfer devices known as charge-coupled devices (CCDs) are used here to study trap behavior at higher temperatures. The CCDs enable measurements of trap emission times of the order of 100 ns and are used around 77 K. The present CCDs are built with a phosphorus-implanted region in a boron-doped substrate. The CCD data should help resolve open questions about the temperature dependence of the trap cross section.

A capture cross section σ of ~ 2×10^{-16} cm^2 fits the present 77 K CCD transport results. A $1/T^4$ dependence for σ agrees with the CCD data for 65 to 90 K. The literature yields cross section values at 17 to 21 K that are in reasonable agreement with this power law extrapolation. Yet, this cross section appears to be too small for an ionized trap. The cross section appears only in the product σv, with v equal to the electron's velocity. The CCD data at long times may be dominated by the retrapping of the transferring electrons. In this case, the electrons are likely to encounter another ionized donor before they achieve thermal velocity. Thus, a larger cross section is deduced when a smaller velocity than the electron's thermal velocity is used.

A random walk model is used to study the repeated trapping, emission, drift, and diffusion of the electrons as they transfer along the CCD. Calculations show that the time-dependent transfer results are sensitive to the capture cross section of the trap. This allows the mechanisms for the temperature dependence of the trap cross section to be clarified.

Lattice Relaxation Effects on Deep Levels: Molecular Dynamics Calculations

Charles W. MYLES and Wei-Gang LI
Department of Physics and Engineering Physics
Texas Tech University
Lubbock, Texas 79409-1051, USA

The effects of lattice relaxation on deep levels associated with substitutional impurities in semiconductors are investigated using a recently developed formalism.[1,2] This approach is a generalization of the Hjalmarson et al. theory[3] and includes the effects of both first- and second-neighbor relaxation. It combines a tight binding Green's function method[1] for including lattice relaxation effects on deep levels with a molecular dynamics technique[2] for determining the amount of relaxation around an impurity.

In this formalism,[1] lattice relaxation is accounted for by characterizing the off-diagonal matrix elements of the defect potential by parameters that depend on the impurity- and host-atom bond lengths. For symmetric, "breathing mode" relaxations, the determinantal equation for the deep levels factors to allow the separate calculation of the A_1 and the T_2-symmetric levels. For either level symmetry, two off-diagonal parameters are needed, one each for the first- and second-neighbor relaxation. By calculating deep levels as functions of these parameters, the effects of varying amounts of relaxation can be systematically explored. To determine these parameters for a specific case, a variation of the inverse bond-length-squared scaling law[4] is used, with the impurity bond length and the first- and second-neighbor host atom positions determined by molecular dynamics.[2] The attractive part of the force which enters the molecular dynamics calculation is computed from the electronic structure using the Hellmann-Feynman theorem[5] and the repulsive part is obtained from a pair potential based on Harrison's overlap interaction.[4]

The results of applying this scheme to several impurities in Si, GaAs, GaP, and other materials are presented and compared with experiment and other theories. These results show that the inclusion of lattice relaxation quantitatively improves the predictions of Ref. 2 in comparision with experiment and that the effects of second-neighbor relaxation are small. Typical results are the predictions that N and O, substitutional for P, and the P antisite defect P_{Ga} in GaP respectively produce deep levels at 2.25 eV, 1.60 eV, and 1.09 eV above the valence band edge. These values are in reasonable agreement with the experimental levels of 2.34 eV (GaP:N), 1.46 eV (GaP:O), and 1.10 eV (GaP:P_{Ga}). For Se and Te in Si, the predicted levels are 0.84 eV and 1.04 eV, which should be compared with the experimental values of 0.86 eV and 1.01 eV.

1. W.-G. Li and C.W. Myles, Phys. Rev. B43, 2192 (1991).
2. W.-G. Li and C.W. Myles, Phys. Rev. B43, 15 April, 1991.
3. H.P. Hjalmarson et al., Phys. Rev. Lett. 44, 810 (1980).
4. W. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).
5. R.P. Feynman, Phys. Rev. 56, 340 (1939).

Recombination-Induced Defect Heating and Related Phenomena

I. N. Yassievich, V.N. Abakumov and A.A. Pakhomov,
A.F. Ioffe Physico-Technical Institute, Leningrad, USSR

The process of multiphonon recombination of electron-hole pairs via defects is accompanied by excitation of defects at high vibrational levels with energies of the order of forbidden gap E_g. This fact is important for understanding of degradation of semiconductor devices and defect annealing. The first extensive theoretical investigation of this problem was made by Wheeks et al [1] who draw attention to essentially nonequilibrium character of defect distribution by vibration energies when multiphonon recombination takes place.

In this work we present a detailed study of the relevant nonequilibrium distribution.

Contrary to the work [1] we take into account a strong dependence of carrier capture and emission rates on the defect vibration energy. Besides that, the value of the carrier energy plays an important part in the energy balance of highly excited defects. We found that strongly excited defects emit hot carriers with mean energy higly exceeding the thermal energy.On the contrary, defects capture predominantly cold (thermal) carriers as they are thermalised very quickly. This process results in a specific "electronic" mechanism of energy relaxation of defect excitations when the concentration of excess free carriers is sufficiently large.

It is also shown that simultaneous action of recombination and generation of electron-hole pairs via highly excited defects induces a special kind of defect diffusion in energy space with a step E_g. As a result, in semiconductors with high concentration of excess carriers the "high-energy tail" of defect distribution by vibration energy falls out considerably slower and may be characterised by an effective temperature $T^* = E_g/k \log(N_c^* N_v^*/np)$, where n, p are the electron and hole concentrations; N_c^*, N_v^* are some effective densities of states.

The theory is applied to the problems of recombination-enhanced defect diffusion and annealing in semiconductors and nonelastic sputtering of solid state under ion irradiation.

The modification of the recombination rate due to defect heating is also discussed.

1. J.P.Wheeks, J.Tully, L.C.Kimmerling *Phys. Rev.* B12, 3286 (1975).

Session PD

New Techniques

Tuesday Evening, 23 July

Rathbone Hall

ONP SPECTROSCOPY OF DEFECTS IN SILICON

Nickolay T. BAGRAEV
A.F.Ioffe Physico-Technical Institute,Leningrad,194021,USSR

Nuclear magnetic resonance (NMR) was used to study optical nuclear polarization (ONP), induced by hyperfine interaction (HFI) between lattice nuclei and various defects in silicon. It has been established that contact HFI is the dominant mode of interaction for shallow donor defects, the dipole-dipole mode being the leading HFI mechanism in the case of deep defects. The mechanism by which ONP spreads over the entire crystal is that of nuclear spin diffusion. Based on these findings, an efficient ONP technique has been developed with applications ranging from characterization of shallow and deep impurity centers, thermal and radiation defects, dislocations and magnetic impurities to the study of metastable properties of deep defects in silicon.

Several examples from recent research results will be reviewed to illustrate the possibilities of the ONP technique, including shallow impurities, rare-earth magnetic centers, and the metastability of deep gold-related centers in silicon. Also demonstrated will be the capability offered by the ONP technique in the control over the concentration, compensation degree and uniform distribution of phosphorus, arsenic, antimony, and bismuth in silicon. Some attention will be given to the application of the ONP technique for determination ofthe shallow donors' ionization energy and fluctuations thereof induced by the Coulombic potentials involved in the formation of donor-acceptor pairs. The application whereby the energy characteristics of magnetic polarons bound on shallow donors can be assessed by controlling the variations in the relationship between the two HFI modes will also be discussed.

The time dependences obtained from the ONP data for reversible transitions made by gold-related centers to the metastable state as a result of optically induced reactions of the form:
$2Au^{0} + h\nu_1 \longrightarrow Au^{-} + Au^{+}$; $Au^{-} + Au^{+} + h\nu_2 \longrightarrow 2Au^{0}$ $(h\nu_1+h\nu_2=E_g)$
will be presented; it will be shown that these dependences fit closely the results reported for gold-related centers from photo-EPR, photoconductivity, and persistent conductivity studies.

ON THE ANALYSIS OF DIGITAL DLTS DATA

CAB Ball and AB Conibear
Department of Physics, University of Port Elizabeth,
PO Box 1600, Port Elizabeth, 6000, South Africa.

Modern digital techniques involving a storage oscilloscope or an analogue to digital converter allow complete capacitance transients obtained in the DLTS experiment to be stored and processed. This provides very much more data than earlier real-time analogue techniques, and can considerably reduce the time needed for the experiment, at the same time providing many more data points.

The analysis of the capacitance transients, which consist of one or more exponential components, is not straightforward. Direct curve-fitting methods are frequently unreliable and although much effort has been spent in this direction, a general method is not available at this time.

Alternative methods involve a number of indirect techniques. The well known DLTS curves of $\Delta C/C$ as a function of temperature may be constructed and the positions of the maxima for different rate windows may be used to obtain the Arrhenius curves of $\ln(T^2/e)$ against inverse absolute temperature in the usual way, allowing single temperature scan DLTS.

In this paper two novel methods of obtaining the Arrhenius curves directly from the capacitance decay curves are presented, one involving a double rate window and the other a digital simulation of the analogue process in a lock-in amplifier. In both cases a point on the Arrhenius curve is obtained for every temperature at which a capacitance decay has been measured.

A major problem in the interpretation of DLTS data is that most capacitance decay curves deviate from the ideal exponential decay. The present work provides a sensitive test for whether a DLTS peak may be identified with a single trap with temperature independent energy and capture cross section. In some cases there is clear evidence for a single trap or a small number of traps in a given peak, while in others traps are not easily resolved.

Trap parameters obtained using real-time analogue methods must be treated with caution in the light of these results.

A REEVALUATION OF ELECTRIC-FIELD ENHANCED EMISSION MEASUREMENTS FOR USE IN TYPE AND CHARGE STATE DETERMINATION OF POINT DEFECTS.

by

W.R. Buchwald[a], H.G. Grimmeiss[b], F.C. Rong[c], N.M. Johnson[d]
H. Pettersson[b], E.H. Poindexter[a]

[a] Electronics Technology and Devices Laboratory, Fort Monmouth, NJ 07703-5000

[b] Department of Solid State Physics, University of Lund, S-22007 Lund, Sweden

[c] GEO-Centers, Inc. Electronics Technology and Devices Laboratory Fort Monmouth NJ, 07703-5000

[d] XEROX Palo Alto Research Center, Palo Alto, CA 94304

Deep level transient spectroscopy and single-shot junction space charge capacitance transient measurements have been used to measure the effects of electric-field on the thermal emission rates of trapped carriers in both GaAs and Si. These measurements reveal apparent inconsistencies when compared to existing field enhance emission (i.e. Poole-Frenkel effect) theory, which casts doubt on the validity of using these measurements for the determination of defect type, (i.e. donor or acceptor), or charge state of the emitting center. Space charge measurements performed on S and Se doped Si reveal field dependencies inconsistent with existing theory for the well known charge state of these centers as determined by IR absorption measurements. DLTS measurements performed on a defect previously observed in MOCVD grown GaAs show unambiguously an electric-field dependent emission rate, but differing quantitative results depending on the method used to extract relevant field dependent parameters. In the case of GaAs, the apparent inconsistencies can be resolved if a temperature dependent field-effect is assumed; but it is shown that these types of measurements are not accurate enough for the unambiguous determination of either defect type or charge state.

X-Ray Spectroscopy following Neutron Irradiation of Semiconductor Silicon.

A. J. Filo, A. Meyer, C. C. Swanson, and J. P. Lavine*
Analytical Technology Division, Eastman Kodak Company, Rochester, N. Y.
*Image Acquisition Products Division, Eastman Kodak Company, Rochester, N. Y.

ABSTRACT

Transition metals form defects in silicon that lead to reduced device performance and yield. Thus, it is necessary to improve techniques that detect metals in silicon. Neutron Activation Analysis has long been used to identify metals and determine their concentration through the measurement of their characteristic gamma-rays. However, lower energy gamma-rays and X-rays (<120 keV) are also emitted by metals that have been irradiated in silicon and it is advantageous to detect these X-rays. This presentation describes the use of a low-energy photon spectrometer (LEPS) system and the gains in metal detection that are possible.

X-rays from elements such as iron, chromium, copper, zinc, and germanium have been detected in silicon wafers with the aid of the LEPS detector. When these elements are irradiated by neutrons, they undergo a neutron capture event to form an unstable isotope that decays by electron capture to a nucleus with one less proton. An example of this would be $^{63}Cu\ (n,\gamma)\ ^{64}Cu \rightarrow\ ^{64}Ni$. The Ni atom then emits the X-rays as a result of the rearrangement of the electron orbitals. The near-surface region of the silicon wafer is probed, since the low-energy X-rays detected by the LEPS are attenuated within the sample. This allows the location of the metal atoms to be isolated to either the front or back surface of the wafer. LEPS offers advantages over conventional activation analysis for several elements; an example of this would be copper. The gamma-rays that are emitted from the activated Cu are 0.511 MeV and 1.345 MeV. The first gamma-ray is due to annihilation radiation of which there are a multitude of sources. The second gamma-ray is emitted with low intensity and occurs where the gamma-ray detector has low efficiency. Therefore, determination of Cu may be difficult. Cu is provided, by the LEPS detector, by detecting the higher intensity Ni X-rays. Other advantages for the technique are the high resolution of the detector, the reduction in background due to the high-energy gamma-ray processes, and the fact that there are fewer peaks associated with the spectrum than there are with a gamma-ray spectrum.

Spin dependent recombination at deep centers in Si-electrically detected magnetic resonance

P. Christmann, M. Bernauer, A. Asenov, C. Wetzel, B.K. Meyer and A. Endrös*

Physikdepartment E 16, Technical Univeristy of Munich, James-Franck Str., D-8046 Garching, F.R.G.

*Siemens AG, Abt. ZFE ME FKE 42, Otto Hahn Ring 6, D-8000 Munich, F.R.G.

The detailled knowledge about the microscopic structure (site and symmetry) of impurities in Si has mainly be supported by electron spin resonance (ESR). Detection of electrically active defects by ESR in a space charge region of a Si p-n-diode brings together two important characterisation techniques, DLTS and ESR. We report on electrically detected magnetic resonance (EDMR) and DLTS investigations in undoped and Pt doped Si n^+p diodes. EDMR-signals at room temperature are obtained as microwave induced voltage changes under constant current biasing the diodes in forward direction. The isotropic resonance at g=2.004 often attributed to dangling bond centers (P_b) is studied in detail by EDMR and DLTS. Isochronal annealings (15 min. 200 < T < 350 ^{0}C) show that the defect behaves very similar as the divacany (G6, G7) in bulk Si.

In Si:Pt pin-diodes for the first time an axial defect is observed by EDMR ($g_{\parallel}$= 1.97, $g_{\perp}$=2.04). Calculations of the recombination current taking into account the energy levels, capture cross sections and concentrations of the Pt defects as obtained by DLTS show that the spin dependent recombination occurs at the Pt donor level.

Nuclear Spin Polarization by Optical Pumping of Impurities in Semiconductors

Kouichi Murakami, Kazusato Hara, and Kohzoh Masuda

Institute of Materials Science, University of Tsukuba
Tsukuba Academic City, Ibaraki 305, Japan

We previously reported for the first time nuclear spin polarization of off-center nitrogen in Si caused by optical pumping. This was detected by electron spin resonance (ESR) measurement in which significant changes in ESR hyperfine lines was observed below 50 K.

In order to clarify the mechanism of nuclear spin polarization of impurities with the hyperfine interaction in semiconductors by optical pumping, we have investigated off-center N in Si, on-center N in 6H-SiC, and off-center N in diamond. The off-center N centers in Si and diamond have bistability, so that optical pumping induces local motion among four equivalent off-center sites and one on-center site at lower temperatures, while the on-center N in SiC does not show such a local motion.

For the on-center N in SiC and off-center N in diamond, there were no significant changes in the hyperfine ESR lines by optical pumping, except shortening in the spin-lattice relaxation time. From the results obtained, we found physical conditions necessary for the nuclear spin polarization induced by optical pumping ; i.e., (1) the nuclear spin memory is retained during an optical pumping cycle , (2) no electron spin memory is realized in the conduction band through the spin-orbit interaction whenthe electron temperature is relatively higher than the lattice temperature, and (3) the spin flip-flop relaxation rate mainly caused by the isotropic hyperfine interaction is enhanced by local motion induced by optical pumping and becomes comparable to the spin-lattice relaxation rate. These results will be discussed in connection with metastability and bistabilty of the off-center N in Si.

Identification af band gap states in semiconductors by deep level transient spectroscopy (DLTS) on radioactive isotopes.

Jon Wulff Petersen and Jakob Nielsen

Institute of Physics, University of Aarhus, DK-8000 Aarhus C, Denmark

Abstract

The deep level transient spectroscopy technique has been applied to silicon doped with radioactive impurities. The appearance or disappearance of features in the spectra following the transmutation of the incorporated radioactive atoms identifies an impurity involved in the centres observed.

Results are presented for Au and Pt diffused in silicon showing that Au occupies the same lattice position as Pt, which from electron paramagnetic resonance (EPR) measurements are known to be an isolated (distorted) substitutional site. The well-known Au and Pt deep donor and acceptor levels are all shown to originate from this type of center.

First results concerning diffused Ir and Os are also discussed.

EXCITED DEFECT ENERGY STATES FROM TEMPERATURE DEPENDENT ESR

C. Kisielowski[1)], K. Maier[1)], J. Schneider[1)], V. Oding[2)]
[1)]Fraunhofer Institut für Angewandte Festkörperphysik,
Tullastrasse 72, D-7800 Freiburg
[2)]A. F. Ioffe Physico-Technical Institute, 194021 Leningrad USSR

Using a simple model which relates the ESR signal intensity of paramagnetic electrons in the ground state of a defect to thermal excitations to higher lying electronic states, we show that the excitation energies can be determined from an Arrhenius plot of normalized ESR signals with high precision. Physically the method bases on thermal population of excited states as the temperature is increased. This causes a reduction of the ESR signal amplitude. In several cases we observed a temperature dependent reduction of the central hyperfine splittings as well as a change of the ESR line widths, too. The reliability of the method is checked by the detection of the $(1s)A_1$ to $(1s)T_2$ and $(1s)A_1$ to $(1s)E$ transitions in Si:P. In 6H-SiC:N and 15R-SiC:N we measured valley-orbit splittings of different hexagonal and cubic lattice sites of the nitrogen donor. Other applications concern hopping processes in plastically deformed Si:P and strongly doped 6H-SiC:N. Measurements on the Ga_{As} antisite defect in GaAs and on the boron acceptor in 6H-SiC are in progress. Numerical values for energies and hyperfine splittings are given in the paper.

MUON STOPPING SITES IN SEMICONDUCTORS FROM DECAY-POSITRON CHANNELING

H. SIMMLER, P. ESCHLE, H. KELLER, W. KÜNDIG, W. ODERMATT, B.D. PATTERSON, I.M. SAVIĆ, J.W. SCHNEIDER, B. STÄUBLE-PÜMPIN, U. STRAUMANN, and P. TRUÖL
Physics-Institute, University of Zurich, CH-8001 Zurich, Switzerland

The lattice positions of implanted positive muons (μ^+) in intrinsic semiconductors (Si, GaAs, InP) have been investigated by muon-decay positron channeling at temperatures ranging from 95 K to 400 K. The positron flux in a solid angle $\Omega \simeq 1.3 \times 10^{-3}$ steradian is recorded with a planar multi-wire proportional chamber. The observed flux distributions exhibit planar lattice steering effects with a width of the order of 0.1°.

In high purity float-zone silicon a muon site transition is observed in the temperature range between 200 K and 300 K. As identified by means of planar simulations, the site is mainly T(Tetrahedral)-like at low temperatures and BC(Bond-Center)-like at high temperatures. For an interpretation of these results, we refer to detailed muon-spin-rotation(μSR)-measurements revealing two different neutral (paramagnetic) muonium states (μ^+e^-) at low temperatures [1]: an isotropic state (Mu, stable up to 250 K) and a <111> axial-symmetric state (Mu*, stable up to 120 K). In comparison to the μSR data, we relate the observed metastable T-like site to the Mu state. The BC-like site is found to be stable for both the neutral (Mu*) and the final ionized charge state and acts as a trapping site for Mu.

In gallium arsenide a similar site transition is observed in the temperature range from 300 K to 375 K, indicating again a metastable T-like site as expected from μSR-data. Point defect cluster-calculations qualitatively agree with our results [2]. However, our experiments indicate a puckered BC-state (rotation around the bond) whereas most calculations assume a well localized BC-site. In the case of indium phosphide, the pattern does not change in the temperature range from 95 K to 300 K. It corrsponds to the BC-like "high-temperature" μ-site. On the other hand, no muonium states could be observed by μSR.

In summary, the measurements strongly indicate a metastable state at a T-like site in pure silicon and gallium arsenide. This position is assigned to Mu. The stable site in silicon, gallium arsenide and indium phosphide is BC-like within the temperature range investigated.

[1] B.D. Patterson, Rev. Mod. Phys. 60 (1988).
[2] See, e.g., C.G. Van de Walle, Phys. Rev. B 39, 10791 (1989).

Local-mode spectroscopy and model study for assessing the role of light defects in III-V compound semiconductors

D. N. TALWAR,* M. O. MANASREH,** D. W. FISCHER,**
S. J. PEARTON,*** and G. MATOUS*
* Department of Physics, Indiana University of Pennsylvania, Indiana, PA, 15705-1087
** Wright Laboratory, Wright Patterson AFB, Ohio 45433
*** AT&T Bell Laboratories, Murray Hill, New Jersey 07974

High resolution local-mode spectroscopy is used as a quantitative diagnostic tool to asses the role of light impurities (viz., Be, C, O, Si, and H) in III-V compounds (GaAs, InP) and related materials such as $Al_xGa_{1-x}As$. In GaAs, the observed localized vibrational modes (LVMs) from Be(Ga) acceptors, C(As) acceptors, Si(Ga) donors, Si(As) acceptors, Si(Ga)-Si(As) pairs, and Si-X (a complex of silicon with a native defect) are evaluated in terms of realistic lattice dynamical calculations.[1)] The results of optical absorption experiments on proton- and deuteron-implanted GaAs and InP will be reported. To predict the role of hydrogen in GaAs:Si,[2)] and to provide an explanation for the oxygen-related defects in GaAs,[3)] the above theoretical results are found significantly important in our comprehensive analysis of the IR and Raman scattering experiments. In $Al_xGa_{1-x}As$, the results of the effects of local environment on the LVMs around light defects reported recently[4)] will be compared and discussed in terms of our model calculations.[5)]

1. D. N. Talwar, M. Vandevyver, K. K. Bajaj, and W. M. Theis, Phys. Rev. B33, 8525 (1986).
2. B. Pajot, R. C. Newman, R. Murray, A. Jalil, J. Chevallier, and R. Azoulay, Phys. Rev. B37, 4188 (1988).
3. J. Schneider *et al.* Appl. Phys. Lett 54, 1442 (1989); H. Ch. Alt, Appl. Phys. Lett. 54, 1445 (1989).
4. H. Ono and T. Baba, Phys. Rev. B42, 11423 (1990).
5. D. N. Talwar and M. Vandevyver, Phys. Rev. B40, 9779 (1989); C. R. Abernathy *et al.*, Appl. Phys. Lett. 57, 294 (1990).

Session PE

Superlattices, Surfaces and Interfaces

Tuesday Evening, 23 July

Rathbone Hall

SPECTROSCOPY OF SHALLOW DONOR IMPURITIES IN GaAs/AlGaAs MULTI-QUANTUM WELLS

Janette L DUNN, Elaine PEARL and Colin A BATES
Physics Department, The University, Nottingham, UK

The spectra observed from silicon-doped GaAs/AlGaAs multi-quantum well structures in experiments such as far infrared photoconductivity contain peaks which have been identified with transitions from the ground state to several excited states of a confined Si impurity[1]. Data is available for impurities in magnetic fields[2] of up to 10 T. Such systems are of particular interest as some of the observed spectral features can be explained in terms of a low-field 'hydrogenic' model, whilst other features are consistent with strong-field descriptions, where Landau-like behaviour dominates.

Details of a theoretical model will be given which can be used to identify some of the observed peaks with transitions from the 1s-like ground state of a hydrogen-like impurity to excited states such as $2p_{\pm 1}$ and $3p_{+1}$ in the low-field picture. The possibility of transitions to final states with angular momentum m = 2, which should be forbidden by simple dipole selection rules, will be considered. In addition, transitions to odd-parity states such as $3d_{+1}$ will be investigated for impurities which are not located at the centre of a quantum well. The theoretical model is an extension of an approach first developed by Greene and Bajaj[3] in which a set of basis states is constructed using Gaussian-type functions in order to introduce strong-field behaviour into the low-field basis states. Approximate eigenstates are then determined using a numerical diagonalisation procedure.

Although some of the peaks in the observed spectra can be explained using the hydrogenic model, further peaks can not be identified in this manner. Most of these remaining peaks will be identified with transitions to so-called metastable states, which are states which do not have a low-field conterpart. A comparison with the analagous situation which arises in bulk Si-doped GaAs samples will be given.

1. Dunn J L, Pearl E, Grimes R T, Stanaway M B and Chamberlain J M, *Mat. Sci. Forum* **65-66**, 117-22, 1990
2. Grimes R T, Stanaway M B, Chamberlain J M, Dunn J L, Henini M, Hughes O H and Hill G, *Semicond. Sci. Technol* **5**, 305-7, 1990.
3. Greene R L and Bajaj K K, *Phys. Rev. B* **31**, 913-8, 1985.

TWO ELECTRON TRANSITIONS FOR SHALLOW DONORS CONFINED IN GaAs/$Al_xGa_{1-x}As$ QUANTUM WELLS

P.O. Holtz and B. Monemar
Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, SWEDEN

M. Sundaram, J.L. Merz, and A.C. Gossard
Center for Quantized Electronic Structures (QUEST), University of California at Santa Barbara, Santa Barbara, CA 93106, USA

The exciton bound to the shallow Si-donor confined in GaAs/$Al_xGa_{1-x}As$ quantum wells (QWs) has been studied by means of selective photoluminescence (SPL) and PL excitation (PLE) spectroscopy. The samples used are grown by Molecular Beam Epitaxy and contain multiple QWs (n=50). Each QW is 100 Å wide and is doped in the central 20% of the QW with Si. The Si concentration is varied in the range 1×10^{16} - 3×10^{17} cm^{-3}. The optimum concentration for our purposes was found to be 5×10^{16} cm^{-3}, for which the PL spectrum was dominated by the free exciton (FE) and the Si donor bound exciton (BE). Upon excitation resonant with the BE peak, a novel satellite line appears in the SPL spectrum. This satellite is interpreted as the two-electron transition (TET) of the bound exciton observed for the first time to the best of our knowledge. The TET is due to the transition from the initial BE state with the donor in its ground state, $1s(\Gamma_6)$, to a final state, in which the confined Si donor is left in the excited $2s(\Gamma_6)$ state. The interpretation of the TET peak is confirmed by PLE measurements, in which the BE peak intensity is strikingly enhanced in the PLE spectrum, when the TET is detected. The observation of the TET yields a very accurate determination of the binding energies of the excited states and is accordingly important information for improvement of theoretical calculations. The obtained transition energy for the $1s(\Gamma_6)$ - $2s(\Gamma_6)$ transition, 10.6 meV, is in excellent agreement with theoretical predictions, 10.6 meV [1], if the appropriate values on the effective masses and dielectric constants are used for the well and barrier materials i.e. different values are used in these two media. This point proved to be important, since a predicted energy separation of 9.9 meV is provided [2], and accordingly significantly divergent from the experimental observation, if the same values on the effective masses and dielectric constants are used for the two media.

[1] S. Fraizzoli, F. Bassani, and R. Buczko, Phys. Rev. B41, 5096 (1990)
[2] M. Stopa and S. DasSarma, Phys. Rev. B40, 8466 (1989)

LOCALIZED VIBRATIONAL MODE ABSORPTION OF SILICON DONORS AND BERYLLIUM ACCEPTORS IN III-V COMPOUNDS : EFFECTS OF DOPING SUPERLATTICES.

R.Addinall and R.C.Newman
Interdisciplinary Research Centre for Semiconductor Materials,
Blackett Laboratory, Imperial College, London. SW7 2BZ, U.K.

A.Mohades-Kassai and M.R.Brozel,
Department of Electrical Engineering and Electronics,
University of Manchester Institute of Science and Technology,
P.O.Box 88, Manchester. M60 1QD, U.K.

V.Mitter and D.McPhail,
Department of Materials, Imperial College, London. SW7 2AZ, U.K.

M.J.L. Sangster
J.J.Thomson Physical Laboratory, University of Reading,
Whiteknights. RG6 2AF, U.K.

A basic problem of investigating the LVM IR absorption of electrically active impurities in III-V compounds is the removal of the strong electronic absorption, particularly at long wavelengths. The standard method used for GaAs, GaP and InP has been irradiation by 2MeV electrons to introduce defects that act as hole and/or electron traps. However, such treatment renders InAs and InSb progressively more n-type and p-type respectively.

An alternative approach is to grow compensated samples with equal concentrations of silicon and beryllium. Measurements can be made on uniformly doped material provided it is marginally p-type, but the acceptor then has a Fano derivative shape, as found in both GaAs and InSb [1] grown by MBE. Another possibility is to grow block-doped nipi structures, but broad absorption lines have been found for InAs structures. The origin of the broadening could be strain arising from the heteroepitaxial growth on GaAs, or the effects of the large internal electric fields. Consequently, we have examined similarly doped homoepitaxial GaAs structures which show LVM lines with fine structure which appears to be related to the internal electric fields. It is shown that the magnitudes of the splittings are then consistent with those expected from the distribution of the dopants, as revealed by SIMS analysis. Some effects of heat treatments which lead to the interdiffusion of dopants will be included.

[1] R.Addinall, R.Murray, R.C.Newman, J.Wagner, S.D.Parker, R.L.Williams, R.Droopad, A.G.DeOliveira, I.Ferguson and R.A.Stradling, Semicon Sci. and Tech. in press (1991)

NEGATIVE U SYSTEMS AT SEMICONDUCTOR SURFACES

Guy ALLAN and Michel LANNOO
Laboratoire d'Etude des Surfaces et Interfaces, URA 253 CNRS
ISEN, 41, boulevard Vauban, 59046 Lille Cedex, France

It is now well established that bulk defects can exhibit negative U behavior. The present work is concerned with the similar problem at semiconductor surfaces, showing that surface bonds should have a strong tendency to behave as negative U systems.

We first present a fairly general argument based on the fact that the effective U is the difference between a pure electronic contribution U_e and another one due to atomic relaxation U_R. We first show that, even for free molecules like H_2, there is strong cancellation between U_e and U_R so that even if U is positive it is much smaller than both separate contributions. Transferring this to bulk semiconductors both are reduced (U_e by dielectric screening, U_R by elastic restoring forces) by the surrounding crystal, so that U can be > 0 or < 0 according to which effect is dominant. However for surface bonds with one free end (like in chemisorption) only U_e will be reduced (the surface dielectric constant is ~ $(\epsilon + 1)/2$) while U_R will be left unchanged. In all such situations one would thus end up with $U_R > U_e$, i.e $U < 0$.

To confirm this we perform detailed tight binding total energy calculations for Au and Cs on (110) GaAs surfaces. We consider adsorption on top of Ga atoms and calculate the bond length and energy versus electron population. We find $U < 0$ behavior in both cases. We are also able to give an interpretation to the S.T.M. observations and to explain why there is pairing of adatoms.

THE STRUCTURE OF GaAs LAYERS GROWN BY MBE AT LOW TEMPERATURE

Zuzanna Liliental-Weber

Materials Science Division, Lawrence Berkeley Laboratory 62/203, Berkeley, CA 94720

GaAs layers grown by MBE at low temperatures (LT-GaAs) have been reported to have very interesting electronic and transport properties. LT-GaAs buffer layers can remove sidegating or backgating of MESFETs by providing excellent device isolation. LT-GaAs used as an active layer can allow one to construct photodetectors with time constants in the femtosecond range. The key to understanding the unusual properties of these novel layers seems to be the incorporation of high concentrations of extra As.

These as-grown layers are very As rich (up to 1.5% of excess As). Electron paramagnetic resonance and optical absorption studies detected As_{Ga} antisite defects in the as-grown low-temperature buffer layers, in concentrations up to 10^{20} cm^{-3}. X-ray diffraction revealed up to 0.15% increase in the lattice parameter of the epitaxial layers. After annealing at 600°C, the excess of As remains the same, but the lattice parameter of the layers decreases to the substrate value.

Crystal structure of these layers is very sensitive to the growth parameters such as: growth temperature and As/Ga flux ratio. With decreasing the growth temperature the higher As concentration can be incorporated and the smaller layer thickness of high crystal perfection can be grown.The layers grown below 200°C show specific structural defects.

In order to understand semiinsulating properties the same layers annealed at 600°C in-situ in the MBE chamber with an As overpressure were investigated. These layers show decrease of the lattice parameter to the substrate value.The reason of lattice parameter change is high density of As precipitates. Their density and their crystallographic structure depends on the growth parameters. Three types of precipitates were determined: cubic As rich phase, which can lead to special ordered structure (for the first time determined in the LT GaAs), hexagonal As, and amorphous precipitates.

Correlation with optical and electrical properties of these layers will be discussed with a special attention to the existing two models which can explain semi-insulating properties of these layers.

Ab initio calculations on effect of Ga–S bonds on passivation of GaAs surface – a proposal for new surface treatment

Takahisa Ohno and Kazumi Wada

NTT LSI Laboratories

3-1, Morinosato Wakamiya, Atsugi-shi, Kanagawa 243-01, Japan

It has been reported that sulfur treatments drastically reduce the surface state density of GaAs. Conventional explanation of this drastic reduction is based on the assumption that the sulfur treatment reduces the number of midgap As antisite states. This assumption, however, has not been justified yet.

One aim of this paper is to show that the passivating effect of sulfur treatments can be explained quite well in terms of the formation of Ga–S bonds on the sulfur-treated surface without any defects or disorder near the surface. Another aim is to propose a new method of surface passivation in which we make use of the III–S bond formation on surfaces and the band discontinuity at semiconductor interfaces.

We have investigated the structural and electronic properties of the sulfur-adsorbed GaAs surfaces using the *ab initio* pseudopotential method. The optimal adsorption site of S atoms is determined, and Ga–S bonds are found to be stably formed on the sulfur-treated surface. Figure 1 presents the electronic structure of the S-adsorbed Ga-terminated GaAs(001) surface having the optimal Ga–S bonds at its surface. It is shown that the Ga–S bonds noticeably reduce the surface state density in the GaAs midgap region, consistent with the experimental results.

Although the midgap surface states disappears, the sulfur treatment can't totally eliminate the surface states of GaAs, that is, there are still surface states near the valence band maximum (VBM). Accordingly, we propose a new method of surface passivation theoretically based on the above results. The essence of our method is to deposit atomic layers of other semiconductors with lower VBM (such as GaP, AlAs and InP) on GaAs surface before the sulfur treatment. We name it the atomic layer passivation (ALP). we have found that the III–S bonds formed on these semiconductors have the passivating effects similar to the Ga–S bonds on GaAs. Therefore, the ALP treatment is expected to shift the pinning surface states downward against the VBM of GaAs by the valence band discontinuity at the semiconductor interface, as schematically shown in Figure 2, and the carriers in GaAs won't see the surface states virtually. We confirm that the passivating effect is enhanced by the ALP method on the basis of *ab initio* calculations. The ALP is a more general concept than the sulfur passivation and can be experimentally achieved.

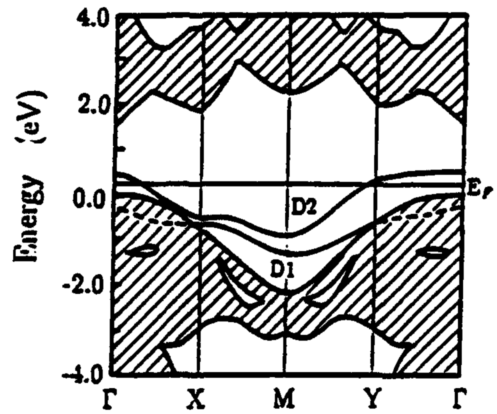


Fig. 1: Electronic structure of the S-adsorbed Ga-terminated GaAs(001)-(1x1) surface.

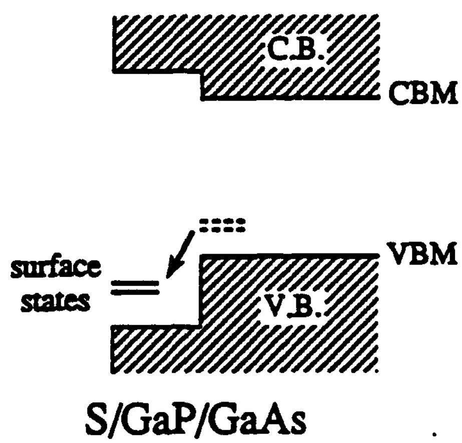


Fig. 2: Schematic band diagram of a S/GaP/GaAs system.

DIFFERENTIAL DIFFRACTOMETRY AND TEM OF InAs/GaSb/GaAs HS GROWN BY MBE.

R.N.Kyutt, S.S.Ruvimov, T.S.Argunova, L.M.Sorokin, P.S.Kop'ev, M.E.Lutsenko

Ioffe Physical-Technical Institute of USSR Academy of Sciencies, Leningrad 194021, USSR.

InAs/GaSb/GaAs HS grown by MBE are an important material for fabrication of FET's with high conductivity of two-dimentional electron channel. This communication deals with structural quality of InAs/GaSb/GaAs HS and superlattices. The study was made via TEM, X-ray topography and diffractometry. On the basis of triple- or double-crystal arrangement with the slit analyzer differential diffractometry permits the distribution of defects to be nondestructively determined.

In practice the variation of $(\Delta d/d)_{\perp}$ and $(\Delta d/d)_{\parallel}$ across the depth of HS has been obtained by using asymmetrical Bragg reflection measurements and by constructing two-dimentional intensity distribution along reciprocal lattice vector $\vec{H}$ /1/. By means of (422) Cu K_{α} the steps in the $(\Delta d/d)_{\parallel}$ distribution have been found to correspond to incoherent interfaces between layers. For GaSb-GaAs interface $(\Delta d/d)_{\perp}$ and $(\Delta d/d)_{\parallel}$ values have been practically equal to each other thus the lattice misfit is highly compensated. With an exception of reflection curves broadening normal to $\vec{H}$ we have separated ω-2 ω -scanning maxima and have compared the halfwidths of them. The analysis of peaks broadening dependency on Bragg angle allowed us to describe the dislocation structure in the layers of HS. TEM cross-sections showed the difference in distribution of defects across the depth of GaSb and InAs layers. While GaSb-GaAs interface was planar and defects were localized near it, InAs-GaSb interface was nonplanar and dislocations formed three-dimentional networks.

To reduce the density of threading dislocations HS contained (50 A°AlGaSb - 50 A°GaSb)$_{20}$ superlattices have been grown. The explanation of obtained diffractometry results lies in lattice misfit being not compensated thoroughly though misfit dislocations being present in the inerfaces of the superlattices.

Thus the comparing of differential diffractometry and TEM results allows the structural perfection of HS to be successively determined.

1.Kyutt R.N., Argunova T.S. 1989 Fizika tverdogo tela 31, 40

STRUCTURAL DEFECTS IN InAsSbP/InAs DH.

T.S.Argunova, R.N.Kyutt, B.A.Matveev, S.S.Ruvimov, N.M. Stus', G.N. Talalakin.

Ioffe Physical-Technical Institute of USSR Academy of Sciencies, Leningrad 194021, USSR.

$InAs_{1-x-y}Sb_xP_y$ alloys lattice matched to InAs (y=2.2x) are materials suitable for fabrication of IR detectors and LED's. Using DH $InAsSbP/In_{1-z}Ga_zAs_{1-q}Sb_q$ grown by LPE we were able to fabricate CW lasers emitting in spectral range 3.0-3.6 μm at temperatures below 160°K /1/. P-InAsSbP/n-InAs/n-InAsSbP DH grown at temperature of InAs plasticity (650-710°C) were studied by X-ray topography, diffractometry and TEM. Triple-crystal diffractometry having higher resolution in ($\Delta d/d$) determination then conventional double-crystal one has been applied. The method involved constructing and analysis of intensity distribution along the reciprocal lattice vector H /2/.

The presence of defects and their distribution over area were revealed by X-ray topography. Diffractometry (422) Cu and Mo K_α measurements permited both $(\Delta d/d)_\perp$ and $(\Delta d/d)_\parallel$ distribution across the depth of DH to be evaluated. Steps in $(\Delta d/d)_\parallel$ distribution indicated the presence of misfit dislocation (MD) networks at interfaces of DH. According to TEM results most of MD's were 60° type with Burgers vector a/2 <110>. A good agreement was shown to observe between MD densities obtained by TEM and calculated from diffractometry data. The highest MD density was at the interface close to InAs substrate: $N_1 \sim 10^4$ cm^{-1}, densities of two other networks were comparable in value: $N_2 = N_3 \sim 10^3$ cm^{-1}. Some of the samples had $N_1 \sim 10^3$ cm^{-1} and $N_2 = N_3 \sim 0$.

The results show the possibility of growing $InAs_{1-x-y}Sb_xP_y/In_{1-z}Ga_zAs_{1-q}Sb_q$ DH ($z \geq 0$, $q \geq 0$) with MD localized at interface near the substrate. This fact is important for long-wave (λ >3 μm) laser fabrication because of MD formation in DH with the active layer mismatched with the InAs substrate.

1. Aydaraliev M. et al 1989 Pis'ma v JTF 15, 49
2. Kyutt R.N., Argunova T.S. 1989 Fizika tverdogo tela 31, 40

^{17}O hyperfine study of the P_b center

J.H. STATHIS
IBM Research Division, T.J. Watson Research Center, Yorktown Heights, NY USA 10598
S. RIGO, I. TRIMAILLE
Group de Physique des Solides, Université Paris VII, Tour 23, 2 Place Jussieu, 75251 Paris Cedex 05
and M. CROWDER
IBM General Products Division, San Jose, CA USA 95193

The P_b center is a silicon dangling-bond pointing into the SiO_2 from the Si side of a Si/SiO_2 interface. It is one of the most important point defects in terms of its influence on silicon technology. In spite of much study, many aspects of its structure remain unknown. In particular, we address here the question of the position of oxygen atoms surrounding the Si dangling bond. Are the nearest oxygen atoms arrayed in specific, well-defined positions with respect to the central silicon, or are their positions random? The former would be the case if oxygen atoms form part of a "cage" or other stabilizing structure around the dangling bond; the latter if the dangling bond points into a random amorphous network.

We have used multi-frequency electron paramagnetic resonance on oxygen-17 enriched Si/SiO_2 interfaces to address this question. Most studies to date of this defect have been performed at 10 GHz or 20 GHz. However, as a general rule, weak hyperfine interactions are better resolved the lower the microwave frequency. This is because the hyperfine splitting (in magnetic field units) is independent of frequency, while some other source of broadening, such as inhomogenous broadening caused by random variations in the defect structure, are proportional to frequency.

We have performed the first S-band (4 GHz) measurements of the P_b center, prepared with either normal- or ^{17}O-enriched oxygen. For the magnetic field normal to the [111] axis, we find the linewidth in the normal samples to be the same at 4 and 10 GHz, confirming earlier assertions that this linewidth results from either unresolved hyperfine or dipolar interactions.

We have further analyzed the line shape of the ^{17}O enriched sample. We will describe our efforts at deconvolving the oxygen hyperfine structure. These allow us to place certain limits on the number and arrangement of oxygen atoms in the vicinity of the dangling bond.

DEFECTS INDUCED BY HIGH ELECTRIC FIELD STRESS AND THE TRIVALENT SILICON DEFECTS AT THE $Si-SiO_2$ INTERFACE

Dominique VUILLAUME and Didier GOGUENHEIM
Laboratoire d'Etude des Surfaces et Interfaces,
URA 253 CNRS, Institut Supérieur d'Electronique
du Nord, 41 Bb. Vauban, 59046 Lille cedex, France.

The interface states created at the <100>$Si-SiO_2$ interface by the injection of electrons under the application of a high electric field (HEF) across the oxide are studied by DLTS. Interface state densities, capture cross-sections and anneal properties of these defects are accurately compared with those of the trivalent silicon defects (the P_b centers). The nature of the HEF-induced defects are discussed and we infer that they are not strictly identical to P_b center, but probably "P_b-like" defects.

The temperature and field dependences of the creation mechanism of these " P_b-like" defects are investigated. We find that three temperature regimes drive the creation of these interface states. At low temperature, <180K, the creation mechanism is not thermally activated. At medium range, 180-300K, an activation energy of 0.1 eV is observed, while at high temperature, >300K, we find a lower activation energy of about 50 meV. The field dependence of the creation mechanism is investigated in the range 8-10 MV/cm. At low temperature stress, we find that the highest oxide fields annihilate the creation of "P_{b1}-like" defects located at around 0.4-0.5 eV below the conduction band, while at lower fields "P_{b0}-like" (at E_c-0.3eV) and " P_{b1} -like" defects are created together. A critical field of about 8.3-8.9 MV/cm is found to be a frontier between these two field dependent behaviors. However, at room temperature stress, this field dependence is not observed and the role of a slow latent formation of " P_{b1} -like" defects during the warm-up of stressed sample from low to room temperature is evidenced.

Session PF

Alloys

Tuesday Evening, 23 July

Rathbone Hall

DOPANT DIFFUSION IN $Si_{0.7}Ge_{0.3}$

Daniel MATHIOT [1] and Jean Claude DUPUY [2]

[1] Center for Microelectronics, MCNC
P.O.Box 12889
Research Triangle Park, NC 27709-2889
(on leave of absence from CNET-CNS, Meylan, France)

[2] Laboratoire de Physique de la Matière, INSA Lyon
20 Avenue Albert Einstein
69621 Villeurbanne Cedex, France

In the last years a lot of efforts have been made to develop new devices taking advantages of the heterojunction formed between silicon and silicon-germanium alloys. Although the fabrication of performing devices would probably involve doping of the material, there is to our knowledge no data concerning the diffusivity of impurities in SiGe materials.
In addition to the technological interest reported above, the study of dopant diffusion in SiGe alloys may also have a more fundamental aspect. Indeed, the basic mechanism of diffusion of dopant impurities in group IV semiconductors is still controversial. Whereas it is now widely accepted that diffusion in Ge is mediated via single vacancies, there is no consensus yet on the majority point defect responsible for diffusion in Si. Thus it is possible that the study of dopant diffusion in SiGe alloys could give some useful informations, and then help to solve the remaining question.
We will report on the results of an experimental study of the diffusion of phosphorus and boron in the $Si_{0.7}Ge_{0.3}$ alloy. We used thick epitaxial layers of $Si_{0.7}Ge_{0.3}$ alloys grown on (100) Si substrates. Dopant was introduced by ion implantation and the anneals were performed between 800 and 1050 °C, for times varying between 30 minutes and 4 hours.
The SIMS profiles clearly indicate a normal diffusion behavior when the dopant concentration is below the intrinsic carrier concentration at the diffusion temperature. On the other hand profiles obtained in extrinsic conditions reveal the same kind of "anomalous" behaviors as observed in pure Si. These results will be critically discussed, and intrinsic diffusion activation energies will be given.

ELECTRON-TRAPPING DEFECTS IN MBE-GROWN RELAXED n-$In_{0.05}Ga_{0.95}As$ ON GALLIUM ARSENIDE

A C Irvine†, L K Howard* and D W Palmer†

† Physics and Astronomy Division, University of Sussex, Brighton BN1-9QH, UK.

* Physics Department, University of Surrey, Guildford, GU2-5XH, UK.

We have studied, by capacitance-voltage measurements and Deep-Level Transient Spectroscopy (DLTS), the electron traps present in 1.5μm-thick, relaxed n-type (silicon doped, $1x10^{16}$ cm^{-3}) $In_{0.05}Ga_{0.95}As$ grown by MBE on an n-GaAs substrate.

We find that the capacitance-voltage data indicate a significant decrease in the apparent carrier concentration close to the heterojunction on the $In_{0.05}Ga_{0.95}As$ side, this suggesting the presence of electron traps in that region. The result has important implications for device fabrication. Our DLTS measurements indicate the presence of two electron-trapping levels in the $In_{0.05}Ga_{0.95}As$ layer, one at E_c-0.55eV and the other at E_c-0.79eV. The shallower level appears to be present in significant concentration only near the $In_{0.05}Ga_{0.95}As$-GaAs heterojunction, while the E_c-0.79eV level is detected throughout the 1.5μm thickness of the layer. DLTS filling-time experiments give evidence of unusual electron-capture characteristics for the traps.

In analysis of the data to determine concentration-distance profiles of the two electron traps, the observed non-uniform apparent doping concentration in the $In_{0.05}Ga_{0.95}As$, coupled with the conduction band discontinuity at the $In_{0.05}Ga_{0.95}As$-GaAs interface, causes difficulty for direct deduction of the concentration profiles of the traps, and to clarify the situation, we have developed a numerical capacitance-voltage simulation program that takes account of the measured energy levels of the traps.

We show the deduced electron-trap concentration profiles and consider how the traps are related to the presence of dislocations known to arise from the $In_{0.05}Ga_{0.95}As$-GaAs lattice mismatch.

ELECTRONIC STRUCTURE OF TRANSITION-METAL IMPURITIES IN $GaAs_{1-x}P_x$ ALLOYS

Luísa M.R. SCOLFARO, Ricardo PINTANEL, and José R. LEITE
Instituto de Física da Universidade de São Paulo
C.P. 20516, São Paulo, 01498, S.P., Brazil

In this work we report self-consistent electronic state calculations for 3d transition-metal (TM) substitutional impurities in $GaAs_{1-x}P_x$ alloys. The electronic state of these systems were calculated within the framework of the molecular cluster model by using the Multiple-Scattering X_α theory. The results reported here were obtained through several 17-atoms clusters centered at the substitutional site. The 3d TM atoms replace the cation in III-V semiconductor compounds (the Ga atom in this alloy). In order to simulate the phosphorus concentration in the alloy some of the four arsenic nearest neighbors around the impurity (the central atom) are replaced by phosphorus. Within the molecular cluster model, if n of the four nearest neighbors atoms are As, then (4-n) atoms are P; therefore, this configuration corresponds to a phosphorus concentration $x=(4-n)/4$ in the alloy. The calculations were performed by including a second shell with the twelve next nearest neighbors Ga atoms in the cluster.

By keeping gallium as the central atom in the cluster (or replacing it by a TM atom impurity) and changing the configuration of the nearest neighbors we simulate the undoped (or doped) alloy for x=0, 0.25, 0.5, 0.75, and 1.

We discuss the results obtained for the undoped $GaAs_{1-x}P_x$ alloy and for Cu and Mn substitutional impurities. We analyse the trends in the impurity electronic states as x ranges from 0 (GaAs) to 1(GaP).

ATOMIC ORDERING IN (110) InGaAs AND ITS INFLUENCE ON ELECTRON MOBILITY

Osamu UEDA and Yoshiaki NAKATA
Fujitsu Laboratories Ltd., 10-1 Morinosato-Wakamiya, Atsugi 243-01, Japan

In most III-V alloy semiconductors, phase separation due to bulk and/or surface spinodal decomposition and atomic ordering on the growth surface, are major issues for thermal stability of the crystals. In particular, atomic ordering in alloy semiconductors grown on (001) substrates have been extensively studied. In most cases, the observed ordered structure is of CuPt type in which sublattice ordering occurs on the (111) planes with doubling in periodicity. It has also been confirmed that ordered (001) InGaP has band gap energies 50-80 meV smaller than those in non-ordered crystals, being very consistent with theoretical calculations.

On the other hand, as previously reported by Kuan et al.[1], a CuAu-I type ordered phase is present in AlGaAs and InGaAs crystals grown on (110) substrates. However, they have only shown transmission electron diffraction patterns corresponding to CuAu-I structure. In this paper, we describe a more detailed study on structural evaluation of ordered MBE-grown InGaAs on (110) InP substrates by transmission electron microscopy. We also report a strong enhancement of electron mobility at low temperature due to the ordering.

In the electron diffraction pattern from the InGaAs, superstructure spots associated with CuAu-I type structure are found. When the tilting angle of the substrate increases up to 5°, the ordering becomes stronger. The ordering is stronger in crystals grown on substrates tilted toward the <001> or the $<00\bar{1}>$ direction than those on substrates tilted toward the $<1\bar{1}0>$ direction. From these results, one can conclude that atomic steps on the growth surface play an important role in the formation of ordered structures. The ordering becomes stronger when the growth temperature increases in the range 360-450°C.

In high resolution TEM images of the crystal, doubling in periodicity of 220 and 200 lattice fringes is clearly observed, which is associated with CuAu-I type ordered structure. Moreover, anti-phase boundaries are very often observed in the ordered regions. It is also found that ordering is not perfect, and that ordered regions are plate-like microdomains lying on planes slightly tilted from the (110) plane. Results of computer simulations of lattice images from both perfectly ordered regions and those including anti-phase boundaries will also be presented and compared with the observed images.

To investigate the electrical properties of strongly ordered (110) InGaAs, we have fabricated InGaAs/N-InAlAs heterostructures with InGaAs channel layer [2]. The measured two-dimensional electron gas mobility from these structures is found to be 153,000 cm^2/Vs at 6K, which is much higher than both theoretical alloy scattering limited mobility [3] and the best result of experiments ever reported for InGaAs/N-InAlAs systems [4]. This mobility enhancement is thought to be caused by supressing alloy scattering due to the formation of ordering.

[1] T. S. Kuan et al., PRL 54, 210 (1985); T. S. Kuan et al., APL 51, 51 (1987).
[2] Y. Nakata, O. Ueda and T. Fujii, Japan. JAP 30, L249 (1991).
[3] Y. Takeda et al., Japan. JAP 24, 1307 (1985).
[4] K.Onabe et al., Surface Sci. 174, 401 (1986).

OBSERVATION OF A TRIVALENT Ge DEFECT IN OXYGEN IMPLANTED SiGe ALLOYS

M.E. ZVANUT*, W.E. CARLOS, M.E. TWIGG, and
R.E. STAHLBUSH
Naval Research Laboratory
Washington, D.C. 20375 USA

Research has recently revealed the potential of SiGe based alloys and superlattices in microelectronic and optoelectronic applications. However, other than the observation of a Ge dangling bond defect (at g=2.02 and about 30G wide) in a-SiGe:H, little fundamental work has been reported on point defects in crystalline Ge or SiGe alloys. In this abstract we report the first paramagnetic resonance observation of an anisotropic Ge dangling bond center in a crystalline SiGe alloy.

Samples used in the current work were 800 nm thick epitaxially grown $Si_{.9}Ge_{.1}$ layers which had been implanted with oxygen to $1.8\times10^{18}cm^{-2}$ and annealed at 900°C in argon. Cross-sectional transmission electron microscopy reveals that the implanted structures consist of an oxide layer buried between regions of heavily damaged SiGe.

Several aspects of the data suggest that the center observed is a Ge dangling bond: 1) with the field parallel to (100) a single, approximately 10G wide line, is observed at g=2.017 (suggesting (111) symmetry) and is absent in similar films without Ge; 2) the angular dependence, somewhat obscured by Si dangling bond defects, is similar to that observed for the GeH_3 radical; and 3) the spin-orbit interaction derived from the g-tensor scales reasonably with that derived from the well-studied Si dangling bond centers. Also, the results of preliminary etch back experiments suggest that the new center is associated with oxide precipitates or the oxide layer; thus, the defect could be a Ge analogue to the P_b center, a Si dangling bond at the interfaces between SiO_2 and silicon.

Experiments are currently underway to determine the roles of oxygen and stress in the formation and structure of this defect. In the presentation more detailed structural models will be discussed and compared to their Si analogues.

*NRC Postdoctoral Fellow

Paramagnetic Resonance of Sn in AlGaAs

M. Hoinkis, J. M. Baranowski,* P. Dreszer,* and E. R. Weber

Department of Material Science and Mineral Engineering, University of California, Berkeley, California 94720
and Materials Science Division, Laurence Berkeley Laboratory, Berkeley, CA 94720

An EPR signal observed during 0.9 eV threshold illunmination has been found in $Al_{0.39}Ga_{0.61}As$ grown by MOCVD. The sample of 100 µm thickness was Sn doped ($n = 3*10^{18}$ cm^{-3}). Resolved hyperfine interaction indicates that this signal arises from Sn with $g = 1.97$, $a = 0.331$ cm^{-1} for ^{119}Sn, and $a = 0.317$ for ^{117}Sn. The isotropic nature of this photoexcited signal and the very large hyperfine interaction allows to conclude that this center is a $S = 1/2$ defect in cubic symmetry with a very localized wavefunction. No persistent photoconductivity could be observed in this sample down to a temperature of 1.4K.

Before photoexcitation, a strong and anisotropic magneto-absorption peak resembling cyclotron resonance was observed at low magnetic fields. During illumination, the Sn-related EPR signal appeared with an integrated intensity corresponding to at least $3*10^{17}$ defects cm^{-3} while the magneto-absorption peak decreased. After illumination at 4.2K the EPR signal disappered and the magnetoabsorption reappeared. These observations strongly suggest that both the magneto-absorption and the EPR signals are due to the same electrons that are either localized on the Sn atoms or in a delocalized state giving rise to the magnetoabsorption signal.

This EPR signal observed here shows strong similarities to signals described by von Bardeleben et al.[1] However, the large hyperfine interaction described here is inconsistent with this signal being due to the hydrogenic donor state of Sn_{Ga} as suggested by these authors. We believe this signal might be caused by a neutral state DX^{*} of the Sn_{Ga} donor, as suggested by Fockele et al.[2] in interpretation of a similar MCDA spectrum. The relatively small intensity of this EPR signal and the lack of persistent photoconductivity seem to be inconsistent with this interpretation; however, the observed strongly anisotropic magnetoabsorption effect indicates the presence of delocalized carriers confined to planes parallel to the substrate surface. We suggest that a variation of the Al concentration during the growth process might result in such local, isolated planes effectively trapping an electron gas, so that no bulk persistent photoconductivity is observed and not all Sn_{Ga} donors can be neutralized.

[1] H.J. von Bardeleben et al., Phys. Rev. B40, 5892 (1989).
[2] M. Fockele J.M. Spaeth, and P. Gibart, Proc. ICPS-20, p. 517 (1990).

* Permanent address: Inst. of Experimental Physics, Warsaw Univ., 00-681 Warsaw, Poland

Session PG

Processing Defects and Defects in Devices

Tuesday Evening, 23 July

Rathbone Hall

NEAR-SURFACE DEFECTS INTRODUCED IN n-GaAs DURING ELECTRON-BEAM DEPOSITION OF Ti and Pt.

F. Danie Auret, G. Myburg, W. O. Barnard, H. W. Kunert and L. Bredell

Physics Departement, University of Pretoria, South Africa

Schottky barrier diodes (SBD's) were fabricated on epitaxially grown n-GaAs by electron beam (EB) deposition of Pt and Ti. The electron fluence reaching the GaAs surface due to emission of electrons from the filament of the electron beam evaporator could be controlled by changing the deposition rate or by using an electron shield. The quality of the SBD's was evaluated by current-voltage and capacitance-voltage measurements and was found to depend on the total electron fluence that the SBD's were exposed to. This in turn was related to the EB induced defects which were characterised by deep level transient spectroscopy (DLTS). The DLTS results showed that the near-surface defects in the case of Ti SBD's were different to those of Pt SBD's, but that the defects introduced further below the surface were the same in both cases. Further, these near-surface defects exhibited a band like energy distribution in the GaAs bandgap.

ION IMPLANTATION INDUCED SHEET STRESS DUE TO MICROSTRUCTURAL DEFECTS IN THIN (100) SILICON FILMS

Jianzhong Yuan, Andrew J. Yencha and James W. Corbett

The Institute for the Study of Defects in Solids
Department of Physics, State University of New York at Albany,
Albany, NY 12222, USA

Detailed measurements of $^{40}Ar^+$ ion implantation induced sheet stress were carried out on thin (100) Si films at doses ranging from 10^9 to 10^{16} cm^{-2} at room temperature. The stress is compressive and increases with dose up to of the order of 2×10^{14} cm^{-2} for 100 KeV $^{40}Ar^+$ implanted at 0.1 $\mu A/cm^2$. After which it decreases and finally attains a constant value, which is approximately 35% of the peak stress value. The peak stress over unit depth decreases as the implantation energy increases, while the dose corresponding to this peak stress increases as the implantation energy increases. RBS/channeling measurements verified that this dose value is less than the implantation critical dose. A model has been established, and a second-order differential equation has been derived that reproduces the stress curve and the well-established amorphization curve of ion implantation.

EFFECTS OF VACANCY-RELATED DEFECTS IN STARTING CZ SI SUBSTRATE UPON THERMALLY-GROWN OXIDE BREAKDOWN FIELD STRENGTH

H. Koya[1], Y. Horioka[1], Y. Furukawa[1], T. Shingyoji[2], H. Suga[2], S. Dannefaer[3], and S. Hahn[4]

1. Japan Silicon Co., Ltd., 314 Nishisangao, Noda-shi, Chiba-ken 278, Japan

2. Mitsubishi Materials Corporation, Central Research Institute, 1-297 Kitabukuro-cho, Omiya, Saitama 330, Japan

3. Department of Physics, University of Winnipeg, Winnipeg, Manitoba, Canada R3B 2E9

4. Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305

Recently, in dynamic random access memory (DRAM) devices, use of storage MOS capacitor needs thin reliable oxides with the lowest defect density of very large integrated circuits. The oxide thickness decreases with increasing bit density of DRAM devices while the total thin oxide area increases, taking into account the margin of sensitivity of sense amplifier and soft error. Therefore, it is very important to identify various causes for poor oxide growth during wafer processing and eliminate (or suppress) the sources. Until now, four different sources have been shown to critically affect quality of thermally grown oxide. They are: 1) surface contamination; 2) charge build-up; 3) surface structure; and 3) substrate characteristics. In the case of substrate characteristics, precipitation sites in silicon decorated by metal precipitates have attracted the most attention as the cause of B mode failures. In this study, we evaluated another substrate related parameter related to crystal growth ("thermal history"). During actual crystal growth process, one of the ways to change the thermal history is to vary the pull speed, which can influence the frozen-in vacancies and the subsequent precipitation.

In this presentation, we will discuss these quite interesting and potentially very important correlations between vacancy-related defect concentration of the starting substrate and dielectric film breakdown strength, and propose possible oxide breakdown mechanisms due to high point defect concentration in the starting Si substrate.

PHOTOLUMINESCENCE CHARACTERISATION OF THE SILICON SURFACE EXPOSED TO PLASMA TREATMENT.

A. HENRY, B. MONEMAR
Department of Physics and Measurement Technology,
Linköping University, S-581 83 Linköping, Sweden.

J.L. LINDSTRÖM
National Defence Research Establishment,
P.O. Box 1165, S-581 11 Linköping, Sweden.

T.D. BESTWICK and G.S. OEHRLEIN
IBM Research Division, T.J. Watson Research Center, Yorktown Heights, N.Y. 10598, USA.

A photoluminescence (PL) study on silicon exposed to various plasmas with the conditions of reactive-ion-etching is reported. Phosphorus- or boron-doped Czochralski silicon crystals were investigated in this work. The plasmas used were argon (Ar), deuterium (D_2), carbon-fluorine (CF_4) or a mixture of 50% argon-50% deuterium (Ar-D_2) and a mixture of 80% helium-20% hydrogen-bromine (He-HBr). Sharp no-phonon PL lines characteristic of transitions at deep neutral defects and known from studies of defects produced by high energy irradiation manifest damage in the crystalline material after the CF_4 plasma with the observation of the G and C lines. Two broad PL lines observed at 1020 and 958.6 meV respectively with a rather large halfwidth of 13 meV are observed after He-HBr plasma treatment on only phosphorus-doped samples and exhibit characteristic of an exciton bound at a complex defect. When Ar is used as a plasma a broad PL band with a halfwidth of about 76 meV is detected at 945 and 935 meV on n-type and p-type material, respectively. In the spectra taken from the silicon surface exposed to a D_2 or Ar-D_2 plasma a very broad PL band (80 meV of halfwidth) is observed at 913 and 900 meV on the n-type and p-type sample, respectively. These broad bands are assumed to arise from recombination processes around extended defects. The excitation power dependence as well as the temperature dependence of the intensity of these PL lines and bands are presented. This PL study shows that different kinds of defects can be induced in the near surface silicon crystal after plasma treatments depending mainly of the composition of the used plasma and they can be observed through various types of radiative recombination processes.

HIGH TEMPERATURE DEFECT-FREE RAPID THERMAL ANNEALING OF III-V SUBSTRATES IN METALLORGANIC CONTROLLED AMBIENT

Avishay KATZ, Aviram FEINGOLD, Steve J. PEARTON, Michael GEVA, Sho NAKAHARA and Ed LANE
AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, NJ 07974, USA

High temperature defect-free rapid thermal annealing of InP and GaAs under protective ambient of tertiarybutylphosphine (TBP) and tertiaributylarsine (TBA) liquid metallorganic precursor vapors, respectively, was executed by means of a load-locked rapid-thermal-low-pressure-metallorganic-chemical-vapor-deposition (RT-LPMOCVD) reactor.

The damage-free annealed surfaces were obtained while heating InP at temperatures up to 700°C under low pressure TBP (50 mTorr), and GaAs at temperatures up to 950°C under low pressure (50mTorr) TBA. These two processes exhibited a significant superior annealing results, compared to RTA under standard inert ambient such as N_2.

Thus, it was concluded that the TBP and TBA provided the necessary partial pressure for the group V without the need to use the hazardous PH_3 or AsH_3 gases. This reduces appreciably the risk associated with the annealing process, and indeed enabled much more efficient process due to the higher decomposition of these metallorganic sources

Study of the gettering stability of internal oxide gettering at different levels of oxygen precipitation in Czochralski silicon

Z Laczik[1], R Falster[2] and GR Booker[1]

[1] Department of Materials,
University of Oxford,
Parks Road, Oxford OX1 3PH, UK
[2] MEMC Electronic Materials SpA,
Novara, Italy

Oxygen precipitation phenomena and the gettering of transition metals by oxide particle related defects have been investigated by Scanning Infra-red Microscopy (SIRM), etching and TEM. A series of Czochralski silicon wafers containing different levels of solute oxygen has been annealed using different heat-treatment sequences to produce oxide particles of equal sizes with number densities in the range of 10^5 to 10^{10} cm^{-3}. Additional heat-treatments were used to produce sub-groups with different oxide particle sizes within each number density group. The range for oxide particle size was 30 nm to 250 nm. Cu, Ni and Fe were subsequently diffused into the specimens. Two different cooling conditions, fast and slow, were used. The specimens prepared this way were then cut into halves and one half was re-heated with cooling conditions opposite to the ones applied previously.

The gettering efficiency was assessed by the 'haze test' and direct observations of the 3-D distribution and morphology of the metal silicide particle colonies were made by SIRM and TEM before and after being re-heated. By comparing the observed structures in specimens with and without this extra heat-treatment the gettering stability was assessed. It was established that the oxide particle size, if above a certain limit, has negligible effect on the gettering efficiency. Also it was found that for effective gettering very low oxide particle number densities are sufficient. A significant difference was observed between the behaviour of the different metals, for example Cu and Ni were completely gettered by oxide particles with number densities of 10^6 and 10^7 cm^{-3} respectively. However for gettering stability, a more complex relationship between oxide particle density and gettering stability was established.

The Study of Interfacial Traps of InP Metal-Insulator-Semiconductor Structure

Lu Liwu* Zhou Jie
(National Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Academia Sinica, P.O.Box 912 Bejing 100083.P.R.China)

Qu Wei Zhang Shengliang
(Institute of Semiconductors, Academia Sinica, Beijing P.O.Box 912. 100083. P.R. China)

Indium Phosphide (InP) is well suited for use in high-frequency and optoelectronic devices by virtue of its high electron mobility and large band gap. However, InP device based on the metal-insulator-semiconductor (MIS) structure are known to possess unstable device characteristics, most noticeable of which is the drift in the drain current of metal-insulator-semiconductor field-effect-transistors (MISFET). The need for an insulating layer in InP devices arises from the fact that most metal contacts on InP have low barrier energies resulting in large leakage current. Several models have been proposed to explain the cause of the current drift . According to these models , the traps that located in the interface between the insulator and InP, and near the interface in the InP can play a significant role in device performance . In this work the interfacial traps of InP MIS structure samples with different insulating layer grown by PECVD (Plasma Enhanced Chemical Vapor Deposition) has been studied using C-V and DLTS techniques. The typical experimental conditions for DLTS measurements are bias voltage Up=-0.1 or -0.2 v, pulse amplitude V=1.8-2.0 v, pulse width Tp=100 μs, and frequency f=23Hz. The measuring temperature range from 77 to 350 k. Experimental results show that the traps are located in the interface between the insulator and InP, and near the interface in the InP. We obtain the deep level parameters associated with the interfacial traps. the origin of these traps might be due to :(1) During the deposition of insulating layer part of P atoms evaporate and form P vacancies in InP surface, (2) Native defects in InP substrate, (3) Irradiation damage induced by plasma during insulating layer growth process.

*Telefax(8601)2562389.

ANOMALOUS DAMAGE DEPTHS IN LOW-ENERGY ION BEAM PROCESSED III-V SEMICONDUCTORS

S. J. Pearton[+], F. Ren[+], T. R. Fullowan[+], R. Kopf[+], W. S. Hobson[+], C. R. Abernathy[+], A. Katz[+], U. K. Chakrabarti[+] and V. Swaminathan[*]
[+]AT&T Bell Laboratories, Murray Hill, NJ 07974, USA
[*]AT&T Bell Laboratories, Solid State Technology Center, Breinigsville PA, 18031, USA

Dry etching processes such as reactive ion etching (RIE) or ion milling typically introduce deep level defects into the semiconductor which compensate the shallow level doping over many hundreds to several thousand angstroms. This depth of damage introduction cannot be explained without invoking rapid diffusion of point defects into the semiconductor. For example, we show using a selectively doped GaAs/AlGaAs heterostructure that ion bombardment with 400 keV O^+ ions leads to damage depths >410Å. The projected range (R_p) of such ions in GaAs is only ~22Å with a straggle (ΔR_p) of ~11Å. Assuming a Gaussian distribution for O^+ ions directly implanted into the sample from the plasma, the oxygen distribution would fall to 10^{-4} of its peak value at $R_p + 3.72\Delta R_p$, ie. 63Å. Channelling of these low energy ions can increase the incorporation depth by several times, but this alone cannot explain the results. Rapid diffusion of point defects created near the surface is required to understand the depth of carrier compensation. Substantial damage depths can be observed even for very low ion energy bombardment (≤150 eV), suggesting that continual reduction of the ion temperature in plasmas may actually be undesirable beyond a certain point because the resulting decrease in etch rate and anisotropy may not be accompanied by significant decreases in damage depth.

A Study of Radiation Induced Defects in Silicon Solar Cells Showing Improved Radiation Resistance

J. W. Peters, T. Markvart, A. F. W. Willoughby
University of Southampton, Highfield, U. K.

ABSTRACT

The effect of irradiation on solar cells fabricated from various types of silicon have been studied by DLTS.

Particular attention has been given to solar cells designed for improved radiation resistance. This cell manifests internal gettering by a region rich in oxygen precipitates - the gettering region - this should remove mobile, primary radiation damage; this principle is already employed to getter heavy metal impurities in silicon circuits.

The solar cell is fabricated on a defect free surface region, the denuded zone. It has been demonstrated that the carriers are reflected away from the gettering region by an electric field, thus improving the collection efficiency. The control of oxygen in this manner allows the effect of oxygen content on the defects produced to be studied.

Initial results of the I-V characteristics of these cells have demonstrated an improved radiation resistance. Results of a DLTS study are reported in consideration of these results.

These results are compared with conventional Czochralski and floatzone solar cells with varying boron and oxygen content. A range of defects have been identified; defects that are more prolific in the conventional cells than the denuded zone cells are linked to radiation damage.

ROLE OF THE DIFFUSIVITY OF Be AND C IN THE PERFORMANCE OF GaAs/AlGaAs HETEROJUNCTION BIPOLAR TRANSISTORS

F. Ren, T. R. Fullowan, J. Lothian, P. W. Wisk, C. R. Abernathy, R. F. Kopf and S. J. Pearton
AT&T Bell Laboratories, Murray Hill, NJ 07974, USA

The achievement of high speed operation of GaAs/AlGaAs heterojunction bipolar transistors (HBTs) requires high doping levels in several of the component layers, in particular the p^+ base. Conventional p-type dopants, like Be, display a concentration-dependent diffusivity which is also a strong function of the n-type doping levels in the adjacent layers. Under most growth conditions, Be from the base can redistribute into these adjoining layers when very high ($>5 \times 10^{19}$ cm^{-3}) p-type doping is attempted. We show that carbon acceptors (C_{As}), which occupy the opposite sub-lattice to Be_{Ga} acceptors, do not show redistribution during growth, even at doping concentrations above 10^{20} cm^{-3}. Moreover Be-doped, HBTs which we subjected to a bias-stress cycle at 200°C show a decrease in DC current gain as a function of time with the bias applied. The rate of this decrease is proportional to the Be doping concentration in the base and further, both base-emitter and base-collector junctions are degraded. We ascribe these phenomena to reverse-bias drift of Be_i^+ from the base into the adjoining n-type layers. These Be interstitials are created during growth when the solid solubility of Be is exceeded. By sharp contrast, there is no significant decrease in gain in C-doped HBTs under the same bias-stress conditions. We attribute this to the absence of mobile interstitial carbon ions due to the high solubility of carbon on the As sub-lattice. Finally, we show that the presence of nearby implant-isolated regions does not contribute to the diffusion of Be, since the device degradation occurs whether or not these damaged regions are present.

Effects of the substrate-epitaxial layer interface on the HFET and MESFET performance.

M. Spector, M. L. Gray, J. C. Licini
and J. D. Yoder

Sidegating and low frequency oscillations are very detrimental to the performance of GaAs MESFETs and AlGaAs/GaAs HFETs. Sidegating is highly enhanced by carbon impurities at the substrate-epitaxy interface. Deep level traps have been associated with low frequency oscillations and light sensitivity of the devices. We have studied the effect of substrate cleaning using ultraviolet-ozone radiation on device performance. The incorporation of a superlattice at the interface as well as variable buffer layer thickness were investigated. Deep level transient spectroscopy was used to identify the traps present in these materials.

The results showed the DLTS peak causing the device light sensitivity can be eliminated by cleaning the interface. This hole trap has an activation energy of 0.5 eV and a capture cross section of $8 \times 10^{-13} cm^2$.

An influence of carbon on intrinsic gettering quality and circuit performance

L.Tesař and J.Fojtášek *)

Paper will describe the influence of carbon on oxygen precipitation behaviour, intrinsic gettering and consequently on yield of devices.

Presence of carbon, and its influence on the electrical properties of silicon is complex still not well understood. Carbon probably causes point defects, and its role is related to the presence of oxygen.

Yield tests (pn junctions) were fabricated on silicon wafers with different carbon concentrations to show the influence of carbon on intrinsic gettering and leakage limited yield. These tests have been compared with tests of standard devices (with IG, limited oxygen etc.). Concentrations of carbon and oxygen were specified closely with help those yield tests.

Next, chips of RAM memory have been fabricated on two groups of wafers during results of yield tests. By comparing yields of RAM memory carbon and oxygen groups, we can see that average yields of carbon wafers were by 10% higher than on standard wafers.

Conclusion

The influence of carbon on oxygen precipitation is as follows:

- The latent nuclei, which are the forerunners of the active defect nuclei, are formed at temperatures higher than about 1200°C while defect nuclei are formed at temperatures lower than about 800°C. Carbon atoms play an important role in transformation of the latent nuclei into the defect nuclei; the carbon atoms attach the latent nuclei at 900°C-1100°C to enhance the stability of the nuclei, and at temperature below about 800°C, the oxygen atoms attach the carbon clusters to form the defect nuclei.
- The enhancement or retardation of the oxygen precipitation (and so defects density in bulk) will depend on the initial carbon concentration, oxygen concentration and on the device fabrication process.
- The oxygen and carbon concentrations must be harmonized with device fabrication process so that we can reach high gettering efficiency (DZ depth, defect density etc.) and excellent circuit performance.
- Carbon has a gettering effect - (Cu,Au)

---

*)1.máje 1000, CS-756 61 Rožnov p.R, Czechoslovakia

Mobility enhanced-diffusion in electron-beam doping of semiconductors

Takao wada, Michihiko Takeda*, Yuso Shinozuka** and Toshiyuki Kondo

Nagoya Institute of Technology, Showa, Nagoya, 466, Japan
*Nagoya Government Industrial Research Institute, Kita, Nagoya, 462, Japan
**Yamaguchi University, 2557, Tokiwadai, Ube, 755, Japan

The mechanism of electron-beam doping(EBD) method in semiconductors has been investigated. In two-layer structures(array II, AII) of overlayer Zn//substrate GaAs(GaSb) and Ge//Si, the surface of the overlayers in contact with the substrates were irradiated with a total fluence of $\sim(5\text{-}10)\times10^{17}$ electrons/cm^2 at 7 MeV, and at 50 °C from an electron linear accelerator. In other cases, Zn sheets($t\simeq0.5$ mm) were sandwiched between 2 GaAs(GaSb) substrates, (AIII, GaAs(GaSb)//Zn//GaAs (GaSb)) and the surfaces of GaAs(GaSb) overlayers were irradiated. Even without annealing, photoluminescence(PL) spectra for AIII substrates(GaAs,GaSb) were observed at 77 K, but for AII substrates no PL was obtained. These results suggested that the carrier lifetimes of the substrates for AIII were larger than those for AII. In the case of Ge//Si experiments for dose rate dependence, the Ge concentrations N_{Ge} in Si EB-doped with the same fluence increased with increasing dose rate, and became a maximum value at the proper rate. And then N_{Ge} decreased in high dose rate regions. This may be due to the shorter lifetimes of carriers, because higher densities of defects are introduced by higher dose rates. In the experiments of Ge//Si irradiated with a given fluence, the relative intensities of $^{74}Ge^+$ ions to $^{28}Si^+$ ions in Si measured by SIMS were obtained as functions of irradiation electron energy E_e(2-9 MeV) and thickness t of Ge sheet. With increasing E_e and t, their curves passed through maximum values at $\sim$5 MeV energy and at $t\sim0.2$ mm respectively, and then they decreased. In the decreasing regions, the carrier lifetimes would decrease with increasing E_e and t, because of increasing defect densities.

The rate of generation G of electron-hole pairs(ehp's) per unit time by an incident electron can be estimated to be about 3.6×10^{23} $cm^{-3}s^{-1}$ for Si during pulse with on electron irradiation. G produces an electron-hole pair concentrations of $n=G\cdot\tau\simeq3\times10^{14}$ cm^{-3}, where τ is lifetime. For an energy-release mechanism, a number of jumps R are obtained as $R=n\cdot\sigma_e\cdot v\cdot\exp\{-(E_C+E_H)/kT\}$ (10^3 for $E_C+E_H\approx0.17$ eV, 1 for 0.3 eV), where σ is cross sections, v the thermal velocity, E_C thermal activation energy for trapping and E_H thermal activation energy of recombination-enhanced defect reaction ($E_H\approx0$ for the Bourgoin mechanism). In the case of Ge//Si, E_H was measured as $\sim$0.3 eV. The effective diffusion coefficients D_{eff} ($\simeq R\cdot(\Delta x)^2/4$, Δx is jump distance) for recombination-enhanced diffusion are estimated to be about 10^{-12}-10^{-15} $cm^{-2}s^{-1}$, being in roughly agreements with the experiments.

ELECTRICAL PROPERTIES OF OXIDATION INDUCED STACKING FAULTS IN N-TYPE SILICON

J. Kaniewski[a,b], M. Kaniewska[a,b] and A.R. Peaker[b]

a) Institute of Electron Technology, Al.Lotników 32/46, 02-668 Warsaw, Poland, b) Centre for Electronic Materials, University of Manchester, Institute of Science and Technology, P.O. Box 88, Manchester, M60 1QD, England

Recently, there has been a great interest in the electrical activity of extended defects because of their significance in limiting process yields. This is particularly important for silicon, where the high temperature treatment as well as oxidation processes can give rise to stacking faults along with other associated extended defects. There has been a considerable amount of work including DLTS measurements on the electrical properties of dislocations in plastically deformed Si.

In contrast to the previous studies, we report the results of DLTS measurements of deep levels in "clean" epitaxial n-type silicon in the presence of the oxidation induced stacking faults (OSFs). The defects were produced in a control way just at the surface. Among the different traps discovered, one of them shows a correlation with the OSF. It is found that if the entire stacking fault is examined, a broad almost featureless DLTS band is observed. If, however, the fault is spatially profiled, the spectrum deconvolutes into the form of DLTS peaks usually associated with point defects. The deep state depth distribution shows quite unambiguously the peak is associated with the Frank partial dislocation bounding the OSF, not the stacking fault plane itself. This state exhibits a distinct energy shift dependent on its position along the partial dislocation. On the other hand, some conditions on the origin of this as well as other traps as related to impurities are presented. Similarities of traps observed to those detected in plastically deformed samples are discussed.

Session PH

Growth Defects

Tuesday Evening, 23 July

Rathbone Hall

EFFECT OF LOW TEMPERATURE GROWTH ON IMPURITY AND DEFECT INCORPORATION IN AlGaAs GROWN BY MOMBE

C. R. Abernathy, S. J. Pearton, D. A. Bohling*, and F. A. Baiocchi
AT&T Bell Laboratories, Murray Hill, NJ 07974
*Air Products and Chemicals Inc., Allentown, PA 18195

We have investigated metalorganic molecular beam epitaxy (MOMBE) growth of AlGaAs at temperatures ≤500°C using trimethyl-amine alane (TMAAl), triethylgallium (TEG), and AsH_3. As expected, Ga-alkyl pyrolysis, and hence gallium incorporation rate, decreases with decreasing temperature so that the Al contact increases from $X_{Al} = 0.25$ at 500°C to $X_{Al} = 0.57$ at 350°C. Similarly, carbon incorporation is enhanced by ~2 orders of magnitude over this temperature range due to the increasingly inefficient pyrolysis of the Ga-C bond in TEG. Additionally, active atomic hydrogen from the TMAAl, which normally are thought to getter the surface alkyls, are possibly less kinetically active at lower growth temperatures. Contrary to what has been observed in other growth methods, low growth temperatures produced a slight decrease in oxygen concentration. This effect is likely due to reduced interaction between Ga alkoxides (inherent in the TEG) and the atomic hydrogen blocked Al species on the growth surface. Surprisingly, the crystalline perfection as measured by ion channeling analysis is quite good, $\chi_{min} \leq 5\%$, even at growth temperatures as low as 400°C. At 350°C, the AlGaAs layers exhibit severe disorder. This disorder is indicative of insufficient Group III surface mobility, resulting in lattice site defects. The disorder also supports our conclusions of kinetically limited surface mobility of all active surface components.

CHARACTERIZATION OF GaAs/AlGaAs HETEROSTRUCTURES GROWN BY OMVPE USING TRIMETHYLAMINE ALANE AS A NEW ALUMINUM SOURCE

W. S. Hobson+, S. R. McAfee*, K. S. Jones**, N. G. Paroskevopoulos*, C. R. Abernathy+, T. D. Harris+, M. Lamont Schnoes+, and S. J. Pearton+
+AT&T Bell Laboratories, Murray Hill, NJ 07974 USA
*Rutgers University, College of Engineering, Piscataway, NJ 08855 USA
**University of Florida, Department of Materials Science, Gainesville, FL 32611 USA

We have investigated the growth of AlGaAs and AlGaAs/GaAs heterostructures by organometallic vapor phase epitaxy (OMVPE) using trimethylamine alane (TMAA) as a new aluminum source. Since the TMAA molecule does not contain a direct Al-C bond, carbon incorporation is expected to be low. Furthermore, TMAA is not susceptible to the formation of volatile Al-O containing compounds which give rise to oxygen contamination in OMVPE-grown AlGaAs using the conventional Al organometallics. A low-pressure (30 Torr) OMVPE reactor was used for the growth with TMAA, triethylgallium, and arsine as the precursors. The epilayers have been characterized by deep level transient spectroscopy (DLTS), photoluminescence (PL) and photoluminescence excitation spectroscopy, transmission electron microscopy (TEM), and secondary ion mass spectrometry (SIMS). DLTS on intentionally Si-doped $Al_xGa_{1-x}As$ ($N_D-N_A \sim 1-9\times10^{16}$ cm^{-3}, $0.2\leq x\leq 0.4$) indicated low concentrations of EL2 ($<10^{13}$ cm^{-3}) and the expected DX center. All other trap concentrations were below 10^{12} cm^{-3}, suggesting that TMAA does not introduce traps associated with oxygen. SIMS measurements verified that the oxygen concentration was below the detection limit of 5×10^{16} cm^{-3}, which is the lowest level achieved in AlGaAs grown by any technique. PL of multiple quantum well structures exhibited narrow linewidths (2.6 meV) and strong intensity for 10 nm GaAs wells and $Al_{0.32}Ga_{0.68}As$ barriers. TEM using two beam $\vec{g}_{200}$ dark field imaging conditions of a superlattice (50X 4 nm GaAs/44 nm $Al_{0.18}Ga_{0.82}As$) revealed abrupt interfaces, the absence of structural defects, and excellent well-to-well thickness uniformity.

OXYGEN BEHAVIOR DURING Si EPITAXIAL GROWTH: RECENT ADVANCES

B. Pivac[a], *A. Borghesi*[b], *M. Geddo*[b], *A. Sassella*[b] *and A. Stella*[b]

[a] *Rudjer Boskovic Institute, P.O.Box 1016, YU-41000 Zagreb, Croatia, Yugoslavia*

[b] *Dipartimento di Fisica"A. Volta", Università di Pavia, I-27100 Pavia, Italy*

Due to its direct influence on mechanical, electrical and structural properties of materials the importance of the oxygen presence in Si matrix is well known . However, the contamination of epilayer, related to the oxygen present in the substrate, is scarcely treated in the literature.

We have shown recently[1-3] that FTIR micro spectroscopy can be a very useful method for obtaining information about the oxygen precipitate formation. An inherent advantage of the method is represented by the detection of aggregation of oxygen precipitates, due to the very small volume explored.

We used a FTIR spectrometer with IR microscope to obtain transmission measurements in the range 5000-700 cm^{-1}. We mapped the samples with a spot of 20 μm nominal diameter. Samples were 200 μm thick Si strips, cut from standard CZ wafers.

It will be shown that oxygen diffuses significantly from the substrate in the epilayer during the epi deposition. However, oxygen diffusion is very different in differently doped substrates. Various combinations of epi/substrate interfaces in materials differently doped were analyzed. For the first time we shall present a direct optical evidence for the oxygen precipitate formation within the epilayer. The optical method will be compared with other methods we used and its comparative advantage will be pointed out.

(1) A. Borghesi, M. Geddo, B. Pivac, A. Sassella and A. Stella, Appl. Phys. Lett. in press

(2) M. Geddo, B. Pivac, A. Borghesi, A. Stella and M. Pedrotti, Appl. Phys. Lett. 57, 1511 (1990)

(3) M. Geddo, B. Pivac, A. Borghesi, A. Stella and M. Pedrotti, Appl. Phys. Lett. 58, 370 (1991)

Defects in MCZ Silicon with various oxygen and carbon content.

Bochkarev E.P.*, Gorin S.N., Petrov G.N.*, Tkacheva T.M.

Baikov Institute of Metallurgy, USSR Academy of Sciences

***Institute "GIREDMET"**

By X-ray diffraction topography (Lang's technique) and high voltage electron microscopy (1 MeV), microdefects have been studied in silicon single crystals Czochralski grown using an applied magnetic field of various types such as axial constant magnetic field (amf) (induction B = 0.07 to 0.32 T); rotating axial magnetic field (rmf) (induction B = 2.5 to 5 mT); or combined magnetic field (cmf), i.e. amf + rmf.

In the longitudinal sections of amf-grown crystals, there is observed a striated distribution of A'-type microdefects . With increasing magnetic field from 0.2 to 0.32 T, the crystals exhibit enhanced inhomogeneity of properties both in longitudinal and transverse sections and an increase of the concentration of optically active oxygen and carbon to values of 2.6×10^{18} cm^{-3} and 5×10^{17} cm^{-3}, respectively.

Applying rmf combined with intentional changes of the thermal conditions in the furnace, enables controling microstructure of the crystals, i.e. obtaining various distribution of microdefects, such as striated pattern; defect-free regions; or regions containing microdefects of only one type, say, A' defects, etc. The content of optically active oxygen may varies in wide limits in such crystals (from 3×10^{17}cm^{-3} to 8×10^{17} cm^{-3}); the concentration of carbon do not exceed 5×10^{16}cm^{-3}.

In cmf-grown crystals, the concentration of oxygen can be varied between 2×10^{17} to 10^{18} cm^{-3} and the carbon content be as small as 2×10^{16} cm^{-3}. It has been shown that the crystal perfection was independent of the concentration of optically active oxygen;

ELECTRON PARAMAGNETIC RESONANCE STUDIES OF LOW TEMPERATURE MOLECULAR BEAM EPITAXIAL GaAs LAYERS

H.J. von Bardeleben and Y.Q. Jia
Groupe de Physique des Solides de l'Université Paris 7,
Centre National de la Recherche Scientifique,

M.O. Manasreh, K.R. Evans and C.E. Stutz
Electronic Technology Directorate (WL, ELRA),
Wright Laboratory, Wright-Patterson Air Force Base,
Dayton, Ohio 45433-6543 (USA)

Low temperature grown MBE GaAs layers have highly improved properties on buffer layers in MOSFET or MESFET devices as compared to conventially grown layers. These modified properties are related to a dramatic change in the native defects. We have undertaken an electron paramagnetic resonance (EPR) study of low T MBE layers as a function of growth temperature, layer thickness and additional n- or p-type doping. Our EPR results show one dominant arsenic antisite donor defect, whose properties are distinctly different from those of the EL2 defect in melt grown GaAs. The concentration of the As_{Ga} defect varies strongly with the growth temperature and can be as high as 10^{19} cm^{-3} for the lowest growth temperature of 200° C. The ionized antisite concentration of $\lesssim 3 \times 10^{18}$ cm^{-3} clearly demonstrates the simultaneous presence of acceptor defects with at least the same concentration. The As_{Ga} defect, which is known to be higly stable in the EL2 configuration, is found to be thermally unstable in the low temperature MBE layers at temperature T $\gtrsim$ 450° C. The variation of the As_{Ga} properties with the growth temperature and subsequent thermal anneal are correlated with optical absorption (2) and transport measurements (3). Finally, we have studied the influence of the substrate on the native defect concentration by comparing layers grown on Si substrates.

REFERENCES

1. F.W. Smith, A.R. Calawa, C.L. Chen, M.J. Maufra and L.J. Mahoney, IEEE Electron Device Letters 9, 77 (1989).
2. M.O. Manasreh, D.C. Look, K.R. Evans and C.E. Stutz, Phys. Rev. B 41, 10272 (1990).
3. D.C. Look, D.C. Walters, M.O. Manasreh, J.R. Sizelove, C.E. Stutz and K.R. Evans, Phys. Rev. B 42, 3578 (1990).

Session PI

Late Submissions

Tuesday Evening, 23 July

Rathbone Hall

DMS WITH Cr^{2+} - UNUSUAL p-d INTERACTION

J. BLINOWSKI[1] and P. KACMAN[2]
[1]Institute of Theoretical Physics, Warsaw University, ul. Hoza 69, 00-681 Warsaw, Poland
[2]Institute of Physics, Polish Academy of Sciences, al. Lotnikow 32/46, 02 668 Warsaw, Poland

In zinc-blende type semiconductors doped with Cr^{2+} the ground state wave functions of the impurity are built predominantly from the wave functions of the orbital triplet $^5T_2$. This ground state is known to suffer a strong, static Jahn-Teller distortion. On the other hand, in the case of Cr^{2+} ions the orbital triplet $^5T_2$ involves one empty t_{2g} one-electron orbital and therefore, as we have shown previously, the p-d interaction Hamiltonian contains additional, non-Heisenberg terms.

In this paper we show that, within the mean field approximation, in cubic DMS with Cr^{2+} content the non-Heisenberg part of the p-d interaction together with the strong static Jahn-Teller effect may lead to a zero-magnetic field splitting as well as to significant modifications of the magnetic splittings for the valence band. The effect reaches a maximum when all Jahn-Teller distortions are oriented along one of the three [100]-type crystalographic directions. When none of these directions is favored the zero-magnetic field splitting vanishes.

The Exchanged-Site Model of DX Centers

T. N. Morgan

IBM T. J. Watson Research Center, Yorktown Heights, NY 10598

I propose a new model for DX centers and show that it is the only model which agrees with DLTS, metastability and ballistic phonon scattering experiments. In this model an As antisite complex, formed from a substitutional donor by the exchange of two adjacent atoms, binds two electrons. This defect is found to be metastable at low temperature in all three charge states, DX^-, DX^0 and DX^+ Further, the model can explain the paramagnetic susceptibility found for filled DX centers, if the electrons are assumed to occupy a spin triplet state. The stability of such a configuration may be attributed to the unusual properties of the antisite complex. Extension of this analysis to the related EL2 defect in GaAs suggests that the normal EL2 state may be $^3T_2(A_2)$ and the metastability of the excited state due, in part, to spin conservation. These possibilities will be discussed.

Electrical and Optical Properties of Titanium, Molybdenum and Tungsten related Defects in Silicon

K. Schmalz (a), H. G. Grimmeiss (b), H. Pettersson (b), L. Tilly (b), and K. Tittelbach (a)
(a) Institute of Semiconductor Physics, PSF 409
O-1200 Frankfurt (Oder), FRG
(b) Department of Solid State Physics, University of Lund, Box 118, S-22100 Lund, Sweden

The samples used were either p^+n- or n^+p-diodes implanted with Ti, Mo, and W, resp.. The transition metals are diffused into the n- and p-regions by heating the samples to 1100 °C for 30 min. Electrical activation of the metals was achievied by rapid thermal annealing at 1200 °C resulting in a concentration of metal related electrically active centers of about $10^{14}cm^{-3}$.
The purpose of this paper is to present optical studies of these centers. The spectral distributions of photoionization cross sections are compared with an investigation of thermal emission and captures rates which enabled us to present the thermodynamic quantities for the transition metal related centers.
For Ti-doped silicon apart from a probably process-induced midgap level, three energy levels were observed at E_c -0.065 eV, E_c -0.295 eV and E_v +0.255 eV at 80 K. Electron excitation processes of the upper levels revealed values of 0.077 eV and 0.268 eV, resp., for the change in enthalpy as well as 2k and -4k, resp., for the change in entropy. The corresponding values for hole excitation processes of the lower energy level are 0.258 eV and 0.5 k. The Gibb's free energy as a function of temperature was calculated for all three levels and found to be in good agreement with the threshold energies of the corresponding photoionization cross section. Only small, if any lattice relaxation effects are expected.
For the Mo- and W-doped silicon the energy levels were located at E_v +0.298 eV and E_v +0.387 eV, resp., at 80 K. In both Mo and W doped samples a midgap level, probably process-induced, was observed. Optical threshold energies of both centers are in good agreement with calculated changes in Gibb's free energy, indicating a negligible lattice relaxation.
Finally, a comparison of our data with previously published results is given in the discussion.

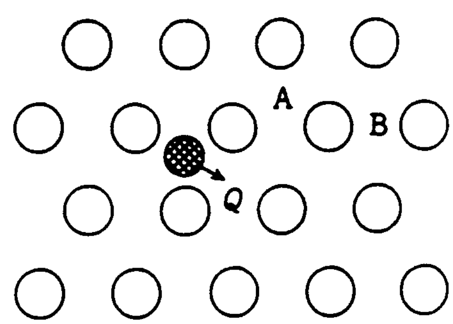
Stability of the Positions of an Interstitial Impurity Atom and the Electronic States in Semiconductors

Yuzo SHINOZUKA
Department of Applied Science, Faculty of Engineering, Yamaguchi University
Tokiwadai 2557, Ube-shi, Yamaguchi 755, Japan

The stability of the positions of an interstitial impurity atom in semiconductors is studied. Positions with high point-symmetry (A and B in the figure) are the candidates, however, whether they are really stable or not depends on the character of the system and their electronic states. Localized electronic states in highly symmetrical systems are usually degenerate and then show the Jahn-Teller (J-T) effect to reduce the symmetry. If the Jahn-Teller active mode(s) contains the displacement Q of the impurity atom, the position must be unstable. Thus, we can obtain useful information on the stable positions of an interstitial impurity atom, without calculating the total energies of the system for different atomic configurations. For example, the tetrahedral interstitial site T_d in the diamond structure is unstable when the electronic state is triply degenerate (T_1, T_2). The hexagonal interstitial site C_{3v} in zincblende structure is unstable for doubly degenerate state (E). Any interstitial site with inversion symmetry, on the other hand, does not show the instability caused by the J-T effect. Th· effe.t of the number of electrons and the spin states are also discussed.

If the stability of the interstitial site for the ground and the excited electronic states is different, the diffusion process of an impurity atom can be accelerated if we excite the impurity atom.

The author thanks Prof. T. Wada of Nagoya Institute of Technology for valuable discussion on diffusion mechanisms in semiconductors.



Effects of Hydrogen in Si-doped AlAs

E. Tuncel, H. Sigg, E. Meier[a], L. Pavesi[b], P. Giannozzi[c],
D. Martin, F. Morier-Genoud, F. K. Reinhart[d]
(a) PSI, Badenerstr. 569, CH-8048 Zurich, Switzerland;
(b) Physics Department, University of Trento, I-38050 Povo, Italy;
(c) IRRMA, PHB-Ecublens, CH-1015 Lausanne, Switzerland;
(d) IMO, EPFL, CH-1015 Lausanne, Switzerland

Electrical properties and absorption bands observed in infrared (IR) transmission experiments of hydrogen plasma exposed Si-doped AlAs epilayers are presented. The results are compared with the better known GaAs:Si-H material. The high quality AlAs:Si and GaAs:Si layers were grown by MBE. Room temperature Hall effect measurements were performed to determine the effects of the hydrogen passivation on the electrical properties of the layers. The electron concentrations in respectively high and low Si-doped AlAs samples were found to be reduced from 2.8x10^{18} cm^{-3} to 1.4x10^{16} cm^{-3} and from 1.5x10^{17} cm^{-3} to 2.2x10^{16} cm^{-3} as a result of the hydrogenation. On the other hand for a GaAs:Si layer with 1.9x10^{18} cm^{-3} carriers, the electron concentration is reduced to 3.2x10^{17} cm^{-3} for hydrogenation under similar conditions. For the high doping concentration, the neutralization efficiency of Si by H is thus 40 times higher in AlAs than in GaAs.

The vibrational properties of the 2μm thick AlAs:Si-H, GaAs:Si-H layers were investigated using high resolution Fourier transform IR-spectroscopy. The bending and stretching modes of the Si_{Al}-H complex were measured for the first time. An absorption peak found at ω_b^{77K}= 890.7cm^{-1} for 77K and at ω_b^{5K}=891.1cm^{-1} for 5K was identified as the Si_{Al}-H bending mode. In effect, this frequency is close to the ω_b found in GaAs:Si-H, where the observed frequencies are 896.2 cm^{-2} and 896.9 cm^{-2} at 77K and 5K, respectively. The integrated absorption of the bending mode in AlAs was found to be 650 cm^{-2}, more than three times the value found for GaAs of 180 cm^{-2}. At 77K, an absorption peak observed at ω_s^{77K}=1607.3cm^{-1} was associated with the Si_{Al}-H stretching mode. This line shifted to ω_s^{5K}=1608.9cm^{-1} for 5K. This is to be compared with an ω_s^{5K}=1717.4cm^{-1} for the hydrogenated GaAs:Si. We could not observe the stretching mode at 77K for GaAs in agreement with results in the literature.

The equilibrium site, vibrational frequency and electronic properties of interstitial H in AlAs:Si have been studied by first-principles calculations in the local density approximation within a supercell approach. We find that the stable configuration for the Si_{Al}-H complex is the anti-bonding-Si site. The lattice undergoes a large relaxation and the Si-As bond is almost broken. These results are similar to those found in GaAs:Si-H and explain the similarity of the bending mode frequencies for GaAs and AlAs. The computed vibrational frequencies with a 32-atoms supercell are for Si_{Al}-H: ω_b=814cm^{-1}, ω_s=1323cm^{-1}; and for Si_{Ga}-H: ω_b=850cm^{-1}, ω_s=1460cm^{-1}. The predicted vibrational frequencies of the Si-H complex are thus similar for the two materials, and are in good overall agreement with the experiments.

INFLUENCE OF FLUORINE ON ELECTRICAL PROPERTIES AND COMPLEX FORMATION IN GaAs

Alexander G.Ulyashin, Yuriy A.Bumay, Vera E.Malahovskaya, Nicolay V.Shlopak
Byelorussian Polytechnical Institute, 65, Lenin avenue, Minsk, 220027, USSR

The effects of fluorine on electrically active defects and implanted ion activation efficiences in semiconductors are of intense scietific and technological interest. In this work we present the experimental results on fluorine effects on electrical properties of Si implanted GaAs and theoretical investigations of complex formation of fluorine with shallow donors (Si) and structural defects in GaAs.

The Si implants consisted of a fluence of $1.5 \cdot 10^{13}$ cm^{-2} at energy of 100 keV. The F ion implantation was then performed at energy of 100 keV with ion doses of $7.5 \cdot 10^{12} - 1 \cdot 10^{15}$ cm^{-2}.
The post-implant annealing (400-800° C, 10 min) and rapid thermal annealing were performed. For comparison dual implantation of Si/N and Si/Ar in GaAs and annealing at the same regimes were carried out. After annealing the implanted layers were characterized by the Hall effect and capacitance-voltage measurements.

It is shown, that dual implantation of Si/F in GaAs leads to decreasing of sheet electron concentration and increasing carrier mobility in implanted layers as compared with single Si implantation and dual implantation of Si/N and Si/Ar in GaAs due to modification of complex formation mechanism and passivation of structural defects. Also partial fluorine passivation of Si_{Ga} donors is found to occur. Quantum chemical calculatins were carried out on cluster - moleculer models by CNDO/2 method. It is shown, that F occupies As sites in GaAs and is a stoichiometrically active like the host lattice atom As. Moreover, the F atom is situated at the antibonding site in GaAs:Si, thus the mechanisms of shallow donor passivation in GaAs by F and H atoms are similar. It is consistent with our experimental results on electrical properties of GaAs implanted layers after dual implantation of Si and F ions.

Session PJ

Defects in Elemental Semiconductors

Wednesday Evening, 24 July

Rathbone Hall

Implantation behaviour of ^{12}B in Si studied by β-NMR

B.FISCHER, W.SEELINGER, E.DIEHL, K.-H.ERGEZINGER, H.-P.FRANK, B.ITTERMANN, F.MAI, G.WELKER, H.-J.STÖCKMANN and H.ACKERMANN
Fachbereich Physik und Wissenschaftliches Zentrum für Materialwissenschaften, W-3550 Marburg, Germany

The behaviour of B in Si was already studied by various methods like EPR, DLTS, channeling, internal friction and profiling measurements. There exist, however, for reasons of low sensitivity no NMR experiments on stable isotopes in order to study B as a diamagnetic centre. The β- radiation detected nuclear magnetic resonance (β-NMR) offers an alternative way. Short-lived ^{12}B probes ($\tau_\beta = 29$ ms) produced by the $^{11}B(d,p)$ reaction in a target foil have been implanted ($E_{imp} = 0 - 450$ keV) in Si crystals. As usual for an in-beam technique the local probe concentration is extremely small ($\lesssim 10^7/cm^3$).

Two types of β-NMR spectra were observed (Fig. 1): A single Zeeman line at the Larmor frequency ν_L and a quadrupole split resonance. The signal depth of the first one corresponds to to the percentage f_s of ^{12}B in normal substitutional sites. f_s was found to increase with increasing temperature (50 - 1000K) with two activation stages depending on the p- or n- type doping level. The high temperature stage (T $\geq$ 300K) has been reported recently by our group /1/.

The quadrupole split resonance corresponds to non-substitutional ^{12}B. The splitting is due to an electric field gradient parallel to the <111> direction with a coupling constant $e^2qQ/h = 360$kHz. Up to now this resonance was only studied at room temperature and in p-type Si for different orientations. Nevertheless, the signal indicates a diffusive motion of non-substitutional ^{12}B within the time window of τ_β.

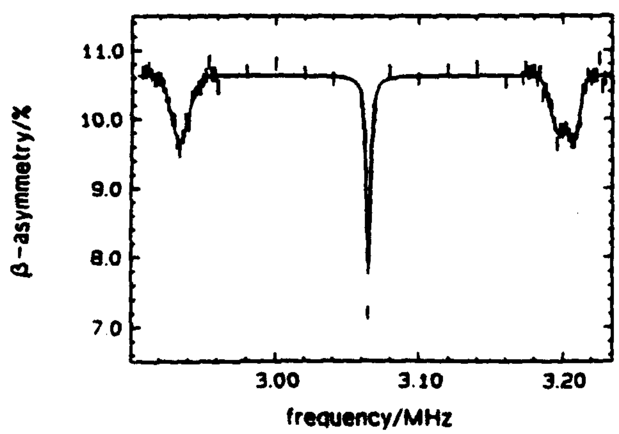


Fig. 1: β-NMR signal of ^{12}B in p-type Si ($2 \cdot 10^{15}$ B/cm^3) at RT. The central line represents ^{12}B at the substitutional site. The quadrupole split resonance, left and right of the central line, is caused by non-substitutional ^{12}B.

/1/ H.Metzner et al., Phys. Rev. B42, 11419 (1990)

A NEW DEFECT OBSERVED IN ANNEALED HIGHLY PHOSPHORUS-DOPED ELECTRON-IRRADIATED SILICON

J.Lennart Lindström
National Defence Research Establishment
P.O.Box 1165
S-581 11 Linköping, Sweden

Bengt G. Svensson
The Royal Institute of Technology, Solid State Electronics
P.O.Box 1298
S-164 28 Kista-Stockholm, Sweden

W.M. Chen
Department of Physics and Measurement Technology
Linköping University
S-581 83 Linköping, Sweden

We report on experimental results from investigations of electron-irradiated and subsequently annealed highly phosphorus-doped silicon (both CZ and FZ material), by infrared spectroscopy (IR), deep-level transient spectroscopy (DLTS) and optical detected magnetic resonance spectroscopy (ODMR). A new defect observed only in CZ-material has been identified and it reaches a maximum in concentration upon annealing between 250-350 ^oC. The defect shows several similarities with the A-center (vacancy-oxygen center) e.g. IR-absorption bands are observed in the region 850-950 cm^{-1} corresponding to different charge-states. The defect is a very efficient electron trap and gives for example rise to a level at E_c-0.51 eV with a capture cross section of approx. 10^{-13} cm^2 according to DLTS measurements. ODMR-results reveal that the defect is A-center-like and contains two phosphorus atoms. We suggest a defect model where an oxygen atom occupies a nearly substitutional site and bonds to two phosphorus atoms. According to this model the defect is anticipated to appear in three different charge states (neutral,single-positive and double-positive). The E_c-0.51 eV level corresponds to the (++/+) level. While the (+/0) level is believed to be in the upper half of the bandgap, indicated by the Fermi-level dependence of the IR bands and the EPR (electron spin resonance) signals.

ATOMIC CONFIGURATION AND INSTABILITY OF N AND N_2 IN DIAMOND, SILICON AND GERMANIUM

A. FAZZIO, C.R.M. CUNHA, A. ANTONELLI and S. CANUTO
Instituto de Física da Universidade de São Paulo
Caixa Postal 20516 - 01498 - São Paulo, Brazil

We investigate the structural properties of substitutional N and N_2 pairs in group IV leasts. Our results for isolated N in the diamonal lattice distorts from the T_d , site along the $<\bar{1}\ \bar{1}\ \bar{1}>$ direction, leaving a broken bond with one carbon atom which retracts in the <1 1 1> direction, in agreement with recent pseudopotential results. We extend the study to N_2 close pairs, and to the Si and Ge crystals. We adopt the cluster model within the "ab-initio" Hartree-Fock LCAO formalism. This approach allows us to determine the iso- and anisotropic hyperfine interactions, which are compared to experimental data.

MULTICONFIGURATIONAL C_i-P_s PAIR DEFECT IN SILICON*

Emir GÜRER†, Brent W. BENSON, and George D. WATKINS
Physics Department, Building 16, Lehigh University, Bethlehem, PA 18015, USA

A fifth configuration of the previously observed[1,2] multistable C_i-P_s pairs was discovered. It introduces two energy levels into the upper half of the band gap after electrical injection of holes at 140K. The measured level position of the acceptor level (-/o) is E_c-0.07 eV whereas the donor level (o/+) is estimated to be at E_c-0.39 eV. Using TSCAP we have assigned the charge states for the energy levels of all five configurations. The conversion kinetics among the configurations was studied under various bias conditions using DLTS. The configurational coordinate (CC) energy surfaces have been constructed for three charge states. The remarkable multiplicity of the various structures of the C_i-P_s pairs is consistent with an ionic model which includes Coulomb interactions between P_s^+ and C_i^-, $C_i^{\cdot}$ or C_i^o at different lattice separations. In addition, the fifth configuration may be a result of a bond rearrangement as evidenced by the lower barrier height for conversion as compared to that of C_i migration. The proposed CC energy surfaces are consistent with two different enhancement mechanisms under electrical injection conditions, namely a charge state effect and a recombination-enhancement mechanism. Our more recent research has found two new multistable defects in silicon doped with As and Sb[3]. These results strongly suggest that carbon and shallow donors form multiconfigurational pairs with a unique combination of Coulomb interaction and multiple bonding arrangements.

†Current address: Zettlemoyer Center for Surface Studies, Sinclair lab., Building 7, Lehigh University, Bethlehem, PA 18015, USA

*Research supported by Office of Naval Research Under Grant No. N00014-84-K-0025.

1. L.W. Song, B.W. Benson, and G.D. Watkins, Phys. Rev. B 33, 1452 (1986).
2. A. Chantre, J.L. Benton, M.T. Asom, and L.C. Kimerling, Mat. Sci. For. Vol 10-12 (1986) p.1111.
3. E. Gürer and B.W. Benson, Mat. Res. Soc. Symp. Proc. Vol 163 (1990) p.295.

DEFECT-IMPURITY COMPLEX FORMATION AT HIGH DONOR CONCENTRATION IN SILICON

A.NYLANDSTED LARSEN and G.WEYER
Institute of Physics, University of Aarhus,
DK 8000 Aarhus C, Denmark

We have recently studied the diffusion behaviour of Ge, Sn, As, and Sb in silicon at high donor (P) concentration and have shown that all of them (except maybe Ge) behave in a similar anomalous way at temperatures of 1000-1050^{0}C. A strong enhancement in the diffusivity by orders of magnitude if found for donor concentrations above $\sim 2\times10^{20}$ cm^{-3}. The diffusion enhancement factor F groups in the following way: $F_{Ge} << F_{As} \lesssim F_{Sn} \lesssim F_{Sb}$. This anomalous behaviour has been successfully modelled within a vacancy-percolation model.

In the case of Sn and Sb in Si, where Mössbauer spectroscopy is possible, the diffusivity enhancement has been found to correlate with the appearance of a new defect complex containing Sn or Sb. A plausible structure of this new defect is a complex of the form Sb-P-vacancy or Sn-P-vacancy.

The present investigation will focus on this new defect complex and we will model its structure and the concentration dependent formation kinetics of the defect complex within the vacancy-percolation model.

PHOTOLUMINESCENCE STUDY OF ALUMINIUM-RELATED DEFECTS IN IRRADIATED SILICON

Vladimir A. BYKOVSKY, Yaroslav I. LATUSHKO*), Vladimir V. PETROV
Laboratory of spectroskopy of semiconductors, Byelorussian State University
Minsk, Lenin Avenue 4, 220080, USSR

We reported photoluminescence (PL) measurements on radiation defekts (RD) in neutron-irradiated Si:Al [1]. In this paper we present the more detailed results of the investigation of PL in neutron- and electron-irradiated Si:Al.

We studied monocrystalline Si:Al with Al content from $1.3*10^{15}$ to $3*10^{17}$ cm^{-3} produced by means of float-zone melting and Czochralski method. The irradiation by 4.5 MeV electrons was carried out at 30°C by fluences (Φ) up to $1*10^{18}$ cm^{-2}, the irradiation by reactor neutrons at $T < 70°C$ by $\Phi \leq 5*10^{18}$ cm^{-2}. PL spectra were recorded at 4.2 K and 78 K with a resolution of ≃ 0.1 meV.

In the PL spectra of the neutron-irradiated Si:Al not only the lines Al1 and Al2 [2] have been discovered but also a number of narrow lines in the spectral region between 0.6 eV and 0.8 eV. These lines are due to electronic transitions on RD which contain Al. We have interpreted the lines at 774.8 meV and 796.1 meV as $1s\Gamma_7(T_2)$-$1s\Gamma_6(A_1)$ and $1s\Gamma_8(T_2)$-$1s\Gamma_6(A_1)$ transitions of the single ionised interstitial aluminium (Al_i) [3]. In the process of isochronal annealing the intensity of these lines decreases and after annealing by $T \geq 200°C$ these lines disappeare. Simultaniously the intensity of following lines increased and after annealing by $T \simeq 200°C$ they reached their maximum value:
622.0, 628.5, 635, 638.9, 651.2, 655.2, 660.9, 667.5, 670, 632.8, 687.1, 688.6, 684.4, 697.3, 702.5, 709.5, 713.4, 719.8, 725.1, 735, 749, 750.9, and 756 meV.

All these lines disappeared after the ≥ 275°C annealing. At about 200°C the diffusion of Al_i starts. Thus this atom can be attributed to the primar RD and build a new complex.

Further annealing at $T \geq 500°C$ leads to the appearance of the 1.12057 eV and 1.1214 eV lines in the PL spectra. Their intensity was maximum after ≃600°C annealing. After annealing by ≃ 675°C these lines disappeared. Thus the peaks are probably caused by a complicated complex, for example a multivacancy including Al atoms.

In the spectra of electron-irradiated samples also the lines at 510 meV (annealing temperatur range 250 - 350°C), 629.7 meV (200 - 475°C), 662.7 and 665.2 meV (100 - 250°C) were recorded. These lines probably are the most simple complexes of primary RD with Al atoms.

1. V.A.Bykovsky, Ya.I.Latushko, V.V.Petrov, Fiz. Tekh. Poluprov. **21**, 2039 (1987).
2. E.Irion, N.Bürger, W.Kürner, K.Thonke, R.Sauer, W.Zulehner, G.Pensl. Appl. Phys. A, **48**, 25 (1989).
3. Ya.I.Latushko, V.V.Petrov, Mat. Res. Soc., **163**, 277 (1990).
4. L.C.Kimerling, in Rad. Eff. in Semicond., (Bristol-London, 1977), 221.

*) now adressee: 4.Physikalisches Institut, Universität Stuttgart
Pfaffenwaldring 57, 7000 Stuttgart 80, FRG

OBSERVATION OF A CONFIGURATIONALLY UNSTABLE DEFECT IN SI

C.A. Londos
University of Athens, Physics Department (Solid St. Section)
104, Solonos Street, Athens 106 80, GREECE

Boron-doped, Czochralski Si Schottky diodes were irradiated in-situ at 80K with 1.5 MeV electrons. DLTS studies were concentrated on a defect state at E_V+0.34eV arising in the spectra after the vacancy migration at ~160K and annealing out at around room temperature. Its corresponding signal exhibits charge-dependent amplitudes. It is stronger when quenching the samples under zero bias than under reverse bias prior to begining the DLTS pulsing. No complementary peaks were detected in the spectra when scanning upwards in the latter case. Surprisingly enough, when the temperature is ramped downwards from T> 180K a peak H* appears irrespective of a previous annealing with or without the application of a reverse bias. When this peak arises the height of the E_V+0.34eV peak is decreased. The peculiarity of the phenomenon lies in the fact that H* has the shape of a peak which is suddenly interrupted during its tracing in the temperature range of~120K. Most remarkably it never emerges in the spectra when scanning upwards.

A model is suggested invoked metastability to account for our observations. Quenching under zero bias conditions set the defect in configuration A. Configura tion B_1 attained when annealing with the application of a reverse bias converts to another configuration B_2 as the temperature going down becomes smaller than 120K. The driving mechanism behind the phenomenon might be substantial entropy changes between the various configurations and along the transformation path. A microscopic picture of the defect is suggested based on the variation of oxygen clustering around the defect core.

ELECTRONIC STRUCTURE OF ISOLATED ALUMINIUM POINT DEFECTS AND DEFECT PAIRS IN Si

H. Overhof
Institut for Theoretical Physics, Physics Department, University of Paderborn. D 4790 Paderborn. Federal Republic of Germany
and
G. Corradi
Research Laboratory for Crystal Physics. Hungarian Academy of Sciences. H-1502 Budapest Pf. 132. Hungary

We use the selfconsistent LMTO-ASA method for the calculation of the electronic structure, total energies and Hyperfine fields for isolated Al point defects and for trigonal Al defect pairs in silicon. Many-body effects are treated in the Local-Density approximation of the Density-Functional theory and the band gap appropriate for Si is obtained using the scissors operator technique. We find that the substitutional Al_{Si}^{-} point defect is thermodynamically stable while the Al_{Si}^{-}-Al_{Si}^{-} pairs, the interstitial Al_{int}^{+} and Al_{int}^{++} states, and the Al_{int}^{++}-Al_{Si}^{-} pairs are are metastable. We discuss in particular the hyperfine interaction (HFI) matrix elements of the Al_{int}^{++}- Al_{Si}^{-} pair in comparison with the Al_{int}^{++} point defect. We show that the HFI matrix elements calculated for an Al_{int}^{++}- Al_{Si}^{-} pair where the Al_{int}^{++} defect is situated on the tetrahedral nearest neighbor interstitial site to the Al_{Si}^{-} substitutional site compare well with the data obtained experimentally for the defect Si-G19 [1],[2] if we change the assignment of the experimental HFI data to the shells in two cases. We show that there are remarkably little changes if the Al_{Si}^{-} in the pair is replaced by a Si atom in agreement with the experimental data.

We discuss results obtained for several trigonal Al_{int}^{++}- Al_{Si}^{-} pairs which differ with respect to the distance between the two Al atoms. These include pairs where the Al_{int}^{++} defect is on the next nearest interstitial site to the Al_{Si}^{-} substitutional site and pairs where the Al atoms are separated by a Si site. We do not find, however, a pair that shows the large HFI interaction with the Al_{Si}^{-} nucleus characteristic for Si G-20, the other trigonal Al_{int}^{++}- Al_{Si}^{-} pair defect observed experimentally by EPR.

[1] G. D. Watkins in: *Radiation Damage in Semiconductors* ed. by P. Baruch, (Academic Press, New York, 1965), p. 97

[2] J. R. Niklas, J.-M. Spaeth, and G. D. Watkins in: *Proc. MRS Meeting* **46**, 237, 1985

INTERACTION AND DYNAMICS OF HIGH-TEMPERATURE DEFECTS IN CARBON-RICH SILICON

Natko B. URLI and Branko PIVAC
Rudjer Boskovic Institute, P.O.B. 1016, 41001 Zagreb, Croatia, Yugoslavia

The Edge-defined Film-fed Growth (EFG) silicon, with carbon supersaturated concentration in excess of 10^{18} cm^{-3}, may be considered as a model system for studies of carbon-dominated processes in thermally treated silicon at high temperature. Contrary to Czochralski silicon, the oxygen/carbon ratio can be changed deliberately and decreased by a factor of one hundred or more by controlling the ambient gases reacting with the silicon melt.

Various EFG polycrystalline silicon ribbons have been annealed isochronally and/or isothermally in the temperature range from 450 to 1250°C. IR spectrometry and the differential technique with oxygen- and carbon-free FZ monocrystalline silicon as a refernce were used to monitor decay and growth of various carbon and SiC microprecipitates and agglomerates. Differences in dynamics of annealing of specific defects in samples of different origin and/or thermal history are explained by different conditions for Si-C, Si-O, C-O, and C-C pairing and precipitation.

A large peak at 800 cm^{-1} in the as received samples, which is present only in the surface layer, depends on the available oxygen during the ribbon growth, and it has been associated with SiC and oxygen aggregates. They start to decompose at a relatively low annealing temperature of 650°C. SiC microprecipitates of various size embedded in bulk of Si give rise to a broad band from 810 to 960 cm^{-1} with well distinguished peaks at 828, 854, and 882 cm^{-1} observable even in the thermally untreated samples. Their concentration remains unchanged up to the 1250°C annealing step, followed then by the same increment, and accompanied by a large decrease in the substitutional carbon concentration. Annealing at 1250°C enhances the interstitial oxygen concentration as well as various C-O complexes in the 1000-1100 and 635-750 cm^{-1} spectral regions. The striking feature of the untreated as well thermally treated samples is the existence of the whole series of bands in the band mode absorption region near the Raman energy down to 400 cm^{-1}. They may be associated with vibrations of carbon pairs with different interatomic distances.

An attempt has been made to correlate changes in electronic quality of different EFG silicon sheets with the existence of specific carbon-based microdefect by combining the results of IR absorption with those of the Hall effect and DLTS measurements.

PHOTOLUMINESCENCE OF EDGE-DEFINED FILM-FED GROWTH SILICON

William D. Sawyer and Jürgen Michel*
Mobil Solar Energy Corporation
4 Suburban Park Drive
Billerica, Mass. 01821-3980

* Massachusetts Institute of Technology
Department of Materials Science and Engineering
Cambridge, Mass. 02139

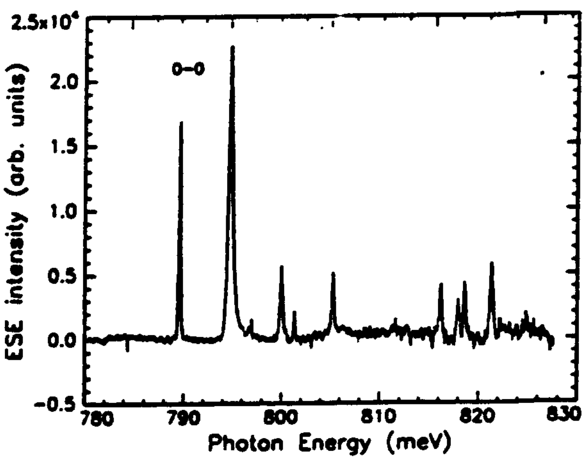
Low temperature photoluminescence measurements are made on edge-defined film-fed growth polycrystalline silicon. Processed and as-grown samples are investigated. The luminescence spectra of the samples are of an intensity similar to the spectra of high quality electronic grade silicon. All of the photoluminescence lines detected are well known from previous investigations of crystalline silicon. The as-grown samples show an unusually intense electron-hole-droplet line. The intensity and energetic half-width of the electron-hole-droplet line varies across the surface and as a function of depth in the samples. Possible causes of enhanced electron-hole-droplet formation are presented.

ELECTRON SPIN ECHO STUDIES ON THE NON-RADIATIVE TRIPLET STATE OF THE Si-SL1 DEFECT.

Ante M. FRENS and Jan SCHMIDT
Department of Physics, Huygens Laboratory, University of Leiden, P.O.Box 9504, 2300 RA Leiden, The Netherlands

It is well known that Electron Spin Echo (ESE) spectroscopy provides a powerful technique to detect and characterize paramagnetic transient species such as photo-induced free radicals and photo-excited triplet states. The method however has scarcily been used for the study of paramagnetic states related to defects in semiconductors.

Here we report the first observation of ESE signals of the non-radiative triplet state of the Si-SL1 defect, the neutral charge state of the O-V pair. In our experiment the ESE signals were induced between the zero-field triplet sublevels, upon pulsed laser excitation at 1.06 μm. By measuring the intensity of the ESE signal as a function of the interval between this laser pulse and the microwave pulse sequence we could establish the dynamic properties of the triplet sublevels. A remarkable finding is that the lifetimes of the sublevels T_x, T_y and T_z differ strongly (800, 250 and 1350 μs respectively) whereas their populating rates are equal.



The ESE technique offers a convenient way to detect the excitation spectrum of this non-radiative defect by monitoring the intensity of the ESE signal as a function of the wavelength of the optical excitation. To this end we used a pulsed laser system tunable between 1-2 μm consisting of a Raman shifter driven by a Nd-YAG pumped dyelaser. In the figure we show part of the excitation spectrum so obtained.

The excitation spectrum is identical to that reported by Wagner et al. (J.Phys.C 18 (1984) L795), obtained via detection of the emission of the oxygen related 0.79 eV (C) defect and it indicates that a strong relation exists between the C defect and the SL1 center. Further experiments are presently in progress to investigate this relation.

ELECTRONIC STRUCTURE AND ELECTRIC FIELD GRADIENT OF A SINGLE Cd IMPURITY IN SILICON

S.J.SFERCO, M.C.G.PASSEGGI* and M.A.CARAVACA***

* *INTEC, Casilla de Correo 91, 3000-Santa Fe, ARGENTINA.*

** *Facultad de Ciencias Exactas y Naturales y Agrimensura, 3400-Corrientes, ARGENTINA.*

Electronic Structure and Electric Field Gradient (EFG) calculations for the single Cd impurity in silicon are presented. Recent Time-Differential Perturbed-Angular-Correlations (TDPAC) experiments raised the interest on the behavior of Cd impurities implanted in silicon. TDPAC measurements show an EFG value different from zero at low temperatures, and a value practically equal to zero at room temperature. The last value is consistent with a tetrahedral environment for the Cd impurity, that is, Cd should be placed either on a substitutional site or on an interstitial-T_d site. On other hand, it is well known that Cd impurities raise deep levels inside the Si gap.

In order to account for the different experimental results for this system, we have performed semiempirical large clusters electronic structure calculations of a single Cd impurity in Si, considering substitutional as well as interstitial-T_d sites for the impurity. EFG was calculated by standard procedures considering contributions from the Si neighbors as well as the valence orbitals for the Cd atom.

Our results show that only the substitutional site is compatible with the experimental information. Interstitial-T_d and related distorted geometries must be rejected because they cannot explain the presence of deep levels in the Si gap. For the substitutional impurity, an "breathing outward" relaxation was considered in order to acomodate the larger size of the Cd atom. This is also consistent with the TDPAC results where a near cubic symmetry is always present. We found a T_2 deep level in the Si gap, mainly vacancy-like in nature. An A_1 resonance in the valence band region, contributed mainly by an A_1 combination of sp^3 Si orbitals pointing to the impurity and the 5s Cd orbitals, is also found.

For a neutral Cd atom, the T_2 level remains unfilled and a Jahn-Teller distortion is then expected. Because of the vacancy-like nature of the level in the gap and the charge transfer from Cd to nearest-neighbors Si atoms, we conclude that substitutional Cd in Si induces a negative vacancy-like (V^-) situation. The Jahn-Teller distortion is proposed to be a negative vacancy-like distortion of the nearest-neighbors atoms of the Cd impurity. Our electronic structure results considering this kind of distortions, allow us to give a very natural explanation for the presence of three deep levels in the Si gap, as well as to calculate an EFG value that is consistent with the experimental value measured at low temperatures. Results for the impurity in different states of charge are also presented.

Electron Paramagnetic Resonance of a Multistable Defect in Silicon

Xuedong Zhan and George D. Watkins
Physics Department, Building #16, Lehigh University
Bethlehem, PA 18015, USA

Three new electron paramagnetic resonance (EPR) centers, Si-L8, Si-L9 and Si-L10, are reported, which we associate with the stable and two of the metastable configurations of a multistable defect recently discovered by DLTS in electron irradiated phosphorus-doped silicon.[1,2,3] Resolved hyperfine structure in Si-L9 and Si-L10 confirms the incorporation of phosphorus in the defect. The results of uniaxial stress studies of the spectra provide strong evidence that carbon is also involved in the defect. Therefore, our EPR results confirm a previously suggested model for the defect as an interstitial-carbon-substitutional-phosphorus pair and provide important clues to the various atomic configurations for the defect.

* Supported by the United States Office of Naval Research under contract No. N00014-84K-0025 and Grant No. N00014-90J-1264.

1. L.W.Song, B.W.Benson and G.D.Watkins, Phys. Rev. B33, 1452(1986)
2. A.Chantre and L.C.Kimerling, Appl. Phys. Lett. 48, 1000(1986)
3. E.Gürer and B.W.Benson, in *Impurities, Defects, and Semiconctors: Bulk and Layered Structures*, ed. by D.J. Wolford, J. Bernholc, and E.E.Haller (MRS Symposium Proceedings Vol.163, Pittsburgh, 1990), p.295

Magneto-Optical Properties of Fe-Al Pairs in Silicon and the Discovery of a new trigonal $(Fe_i\text{-}Al_s)^0$ Pair.

S. Greulich-Weber, A. Görger, J.-M. Spaeth, and H. Overhof

Fachbereich Physik, Universität Paderborn, Warburger Str. 100, D-4790 Paderborn, FRG

Iron-aluminum pairs in silicon are investigated with conventional and optically detected electron paramagnetic resonance (optically detected EPR). For the trigonal and orthorhombic pairs known from previous EPR measurements [1, 2] we found for the first time optical absorption bands by measuring the magnetic circular dichroism of the absorption (MCDA). Trigonal pairs absorb in a sharp band at 0.78 eV followed by a structured continuous absorption at higher photon energies up to 0.97 eV. Orthorhombic pairs have sharp transitions at 0.875 eV, 0.997 eV, 1.01 eV and 1.03 eV. Direct experimental evidence is presented for the configurational bistability of both pairs by showing that the MCDA of the trigonal configuration can be transformed into that of the orthorhombic configuration by the combined effect of light and temperature. The MCDA spectra and pair configurations were correlated by MCDA-detected EPR measurements. A new trigonal pair was discovered by conventional EPR having the same EPR intensity as the known one [1]. It has $g'_{\parallel} = 8.395$ and $g'_{\perp} = 1.076$. The effective spin of both trigonal centers is shown to be S' = 1/2 by MCDA techniques, that of the orthorhombic pair at low temperature is S' = 1/2. The new trigonal pair has a slightly higher ^{27}Al hyperfine interaction compared to the known one [1]. Total energy calculations of various $(Fe_i\text{-}Al_s)$ pair configurations in the local spin density approximation of the density functional theory confirm the stability of two trigonal pairs with different $Fe_i^+\text{-}Al_s^-$ separations. Fe_i^+ is always on a tetrahedral interstitial site, while Al_s^- is nearest neighbor allong <111> in one pair, second nearest neighbor in the other one with one silicon lattice site in between. We do not find stability for the two trigonal configurations proposed by Kimerling et al. [3] for $(Fe_i\text{-}In_s)^0$ pairs. The experimental ^{27}Al hyperfine interactions of the two trigonal pairs agree with the theoretical data for the calculated stable configurations.

[1] J.J. van Kooten, G.A. Weller, C.A.J. Ammerlaan, Phys. Rev. B 30,4564 (1984)
[2] W. Gehlhoff, K. Irmscher, U. Rehse, Material Science Forum, 38-41,373 (1989)
[3] C.C. Kimerling, M.T. Asom, J.L. Benton, P.J. Drevinsky, C.E. Caefer, Materials Science Forum 38-41, 141 (1989)

EPR Studies of NTD-produced As Donors in Isotopically Enriched ^{74}Ge Single Crystals

V.S. Weiner, University of Chicago

It is well known that EPR spectra in Ge are drastically broadened by the presence of ^{73}Ge isotopes, due to their large nuclear spin and magnetic moment. Reduction in the isotope content has been shown [1] to result in a remarkable narrowing of the hyperfine linewidth of shallow donor ([As] ~ 5.10^{15} cm^{-3}) spectra. In the present study, we describe the resolved spectra of As-donors in Ge with the ^{73}Ge isotope content reduced to 1%. The crystal was prepared by the Czochralski method pulling from ^{74}Ge-enriched melt, with subsequent irradiation by slow neutrons, producing the $^{74}Ge + n^{0} \longrightarrow {}^{75}As$ transmutation. The As donor concentration obtained was $(1.85 \pm 0.08)\ 10^{16}$ cm^{-3}. The EPR spectra reveal for the first time well resolved structure arising from exchange interactions between the homogeneously distributed As-donors. The linewidths are highly sensitive to orientation. For H //[100], the spectra are described by an effective Hamiltonian of the form:

$$\mathcal{H} = g_{100}\mu_B\, H\cdot\sum_n S_n + \frac{A}{n}\sum_n S_n\cdot\sum_n I_n$$

where n = number of interacting donors (in a "cluster") and $S_n = 1/2$, $I_n = 3/2$. The line intensities follow the binomial distribution expected for the probability of a "cluster" of n donors which are homogeneously and randomly distributed. The sharp well resolved EPR lines observed in this study provide promise of greatly improved EPR studies of defects in such isotopically enriched crystals.

[1] D.K. Wilson, Phys. Rev. A134, 265 (1964).

Session PK

H in Elemental Semiconductors

Wednesday Evening, 24 July

Rathbone Hall

HYDROGEN EFFUSION IN DOPED MONOCRYSTALLINE SILICON. ROLE OF THE SURFACE DEFECTS ON THE HYDROGEN DESORPTION PROCESS.

Philippe de MIERRY, Richard RIZK, Jean-Claude PESANT, Dominique BALLUTAUD et Marc AUCOUTURIER.
Laboratoire de Physique des Solides, C.N.R.S., 1 Place Aristide Briand, 92195 Meudon, FRANCE.

Hydrogen (deuterium) effusion experiments on plasma deuterated n- and p-type crystalline silicon (10^{14}, 10^{16}, 10^{18} cm^{-3}) are performed, in connection with secondary ion mass spectroscopy (SIMS). The processes which may influence the evolution of the effusion rate, such as the primary rupture of the hydrogen bonds, the diffusion of the hydrogen species to the surface, and the surface recombination of hydrogen to form H_2, are investigated.

Several effusion experiments, either by linear or by isothermal heating, allow the identification of the rate limiting process. In particular, the role, in the effusion process, of the damage surface layer due to the plasma, is examined. The deuterium flow is measured for different isothermal effusions and for different chemical surface treatments and etchings. Results are compared with SIMS deuterium profiles performed prior and subsequently to the isothermal effusion experiments. The depletion or accumulation of deuterium at the surface, as detected by SIMS on the profiles, show that the role of the surface defects due to plasma deuteration is essential to explain the desorption behaviour of hydrogen. These defects are traps for hydrogen diffusing species. Different plasma deuteration conditions are studied.

The linear heating effusion spectra show two main effusion peaks, the temperature and intensities of which are dependent primarily on the dopant type and dopant rate. The two peaks are shifted toward low temperature when the dopant level is increased, the shift being higher for p-type than n-type silicon. The dependence of the effusion spectra on the dopant type, dopant level and heating rate is then discussed in the light of the deuterium bondings and their thermal stability.

EFFECT OF MULTIPLE TRAPPING ON HYDROGEN DIFFUSION IN SILICON

Jeffrey T. BORENSTEIN[a], James W. CORBETT[b] and Stephen J. PEARTON[c]

[a] Mobil Solar Energy Corporation, 4 Suburban Park Drive, Billerica, MA 01821
[b] Physics Department, SUNY at Albany, Albany NY 12222
[c] AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill NJ 07974

The multiple trapping of hydrogen atoms at shallow acceptor sites during plasma hydrogenation of silicon is shown to explain several features of the resulting H diffusion profile. In heavily-doped p-type silicon, the plateau in the SIMS hydrogen profile at the acceptor concentration is preceded by a high concentration plateau near the surface. We demonstrate that this plateau can be explained by multiple trapping of hydrogen atoms at acceptors near the surface, and that the multiple trapping process appears to terminate after the agglomeration of four H atoms at the acceptor sites. The reaction cross-section for multiple trapping appears to be much lower than for the initial trapping of a single H atom; this is consistent with initial ionic capture of H^+ at the negatively-charged acceptor site, followed by neutral multiple capture. The formation of hydrogen dimers, dominant in the case of high resistivity Si, may still be important in the high-concentration near surface profile seen in heavily-doped silicon.

EVOLUTION OF HYDROGEN IN IMPLANTED SILICON

James W. Corbett and Igor V. Verner*

The Institute for the Study of Defects in Solids
Department of Physics
The State University of New York at Albany
Albany, NY 12222, USA

A possible mechanism the formation of a plateau on the profile of hydrogen in p- and n-type silicon is proposed. This mechanism is based on the concept of a long-scale correlation diffusion which strong depends on the type of reactions that occur between hydrogen atoms and impurity (boron or phosphorous) atoms. These reactions can stimulate arising of concentration fluctuations at two points of instability. Diffusion of fluctuations may be a reason for plateau formation. Correlation radius of fluctuations (l_{corr}), i.e. maximum length on which changes at one point can influence on the situation at the other point of the media, is proportional to diffusion coefficient of hydrogen (D) and to the kinetic coefficient (μ) corresponding to the reaction (between hydrogen and impurity atoms) with the lowest value of the rate: $l_{corr} \sim \sqrt{(D/\mu)}$. For the case of p-type silicon calculations were made for proposed scheme of interactions between hydrogen and boron. Values of the l_{corr} have been found to be proportional to the length of the plateau.

It was shown that the distribution (type of profile) of hydrogen depends on temperature and total concentration of impurity. Using methods of fractal approach it is shown that the critical topological dimension of space bellow which fluctuations can not arise exist.

*Permanent address: Physics Department, Moscow Institute of Electronic Technology, Moscow 103498, USSR.

INTERSTITIAL HYDROGEN AND {H,B}, {H,C}, AND {H,Si} PAIRS IN GERMANIUM

Dj.M. MARIC and P.F. MEIER

Physik-Institute, University of Zürich, 8057 Zürich - Switzerland

S.K. ESTREICHER

Department of Physics, Texas Tech University, Lubbock TX 79409-1051

The interactions between interstitial hydrogen and substitutional B, C, or Si in crystalline Ge have been studied at the *ab-initio* Hartree-Fock level in several hydrogen-saturated clusters. Large basis sets were used whenever possible, and corrections for relativistic effects were included.

The stable and metastable structures of the $\{B,H\}$ complex in Ge have been calculated and compared to the well-known $\{H,B\}$ pair in Si, obtained at the same theoretical level. Possible reasons why hydrogen passivation of B is less efficient in Ge than in Si are proposed.

The formation of $\{H,C\}$ and $\{H,Si\}$ pairs in Ge has also been studied. The equilibrium structures and energetics of several configurations with trigonal symmetry are discussed. The relative depths of these traps for H are compared to the bond-centered and tetrahedral interstitial configurations of hydrogen in perfect Ge.

The work of SKE was supported by the grant D-1126 from the R.A. Welch Foundation and a grant from the Advanced Technology Program of the State of Texas.

CHARGE STATES OF DONOR-HYDROGEN PAIRS IN *c*–Si: A FRAGILE BALANCE

S.K. ESTREICHER

Department of Physics, Texas Tech University, Lubbock TX 79409-1051

C.H. SEAGER and R.A. ANDERSON

Sandia National Laboratories, Albuquerque, NM 87185

The debonding rates of hydrogen-passivated shallow donors in silicon have been observed to be very sensitive to the concentration of majority and minority charge carriers. A theoretical study of the stable and metastable configurations of the $\{P, H\}$ and $\{As, H\}$ pairs in the 0 and +1 charge states has been carried out at the approximate *ab-initio* Hartree-Fock level (PRDDO).

The results of these calculations imply that the lowest-energy configuration in the zero charge state is the highest-energy configuration in the positive (+1) charge state, and vice-versa. This bistability implies that the hydrogen passivator cannot remain in place upon change of charge state, whether $0 \longrightarrow +1$ or $+1 \longrightarrow 0$: it can be recaptured, but can be released as well.

Quantitative differences in the potential energy surfaces of $\{P, H\}$ and $\{As, H\}$ are qualitatively consistent with the observed differences in the temperature dependence of the debonding rates of $\{P, H\}$ and $\{As, H\}$.

The work of SKE was supported by the grant D-1126 from the R.A. Welch Foundation and a grant from the Advanced Technology Program of the State of Texas. CHS and RAA are supported by the US Department of Energy under contract number DE-AC04-76DP00789.

RIGID ROTOR IN A TETRAHEDRAL FIELD: AN APPLICATION TO (H,Be) AND (D,Be) IN SILICON

Kevin R. MARTIN, W. Beall FOWLER, and Gary G. DeLEO
Physics Department, Lehigh University,
Bethlehem, PA 18015, USA

We have begun to construct a theoretical framework for the analysis of rotational tunneling systems in tetrahedral symmetry. As a first step, we have calculated the energy levels of a rigid rotor in a two-parameter tetrahedral field in a manner reminiscent of the early calculation by Devonshire[1] of a rigid rotor in an octahedral field. The potential is taken as a linear combination of the first two non-constant spherical harmonics compatible with tetrahedral symmetry, one each from $l = 3$ and $l = 4$. Two parameters K and C measure the strength and shape of the potential, respectively. The Schrodinger equation is converted into dimensionless form and the energy eigenvalues are found as functions of K for selected values of C. An expansion in terms of spherical harmonics through $l = 12$ is used for the wavefunctions. We have applied this model to the experimental IR spectra[2] of the (H,Be) and (D,Be) acceptor complexes in silicon. We find that the spectra are incompatible with this "hindered rotor" model, at least in the sense of a diatomic molecule in rotation either about its center of mass or about the heavy atom, because unreasonably small bond lengths[3] for the complex would be required to fit the experimental data. We suggest that alternative types of hindered rotation should be considered.

1. A. F. Devonshire, Proc. Roy. Soc. A153, 601 (1936).
2. K. Muro and A. J. Sievers, Phys. Rev. Lett. 57, 897 (1986); R. E. Peale, K. Muro, and A. J. Sievers, Phys. Rev. B41, 5881 (1990).
3. Vanessa Gates and Gary G. DeLeo (unpublished).

This research was supported by the U. S. Navy Office of Naval Research, Contract No. N00014-89-J-1223.

Electron Spin Resonance Study on Hydrogen Passivation of Donors in Silicon

Kouichi Murakami, Shigeru Fujita, and Kohzoh Masuda

Institute of Materials Science, University of Tsukuba
Tsukuba Academic City, Ibaraki 305, Japan

Hydrogen in phosphorus-doped silicon and off-center nitrogen-doped silicon has been investigated, monitoring shallow donor P and deep donor N by electron spin resonance (ESR) at low temperatures ranging from 4 to 100 K. In particular the ESR linewidth of P donor is expected to give information about H through the Fermi contact hyperfine interaction between hydrogen nucleus and donor electrons.

The P donors are partially passivated even at exposure times longer than 60 min, when the decrement is 35°. On the other hand, the off-center N is completely passivated at a time of 30 min. It is clear that for comparable hydrogeneration conditions, passivation of the deep donor off-center N is pronounced than for the shallow donor P. The off-center N is trigonally distorted with C_{3v} symmetry about the <111> axis, so that H is presumably located on the largely distorted bond between N and Si, i.e., bond center like for shallow acceptors.

We found changes in P-donor ESR linewidth by hydrogen passivation. Annealing of the hydrogen passivated sample at 400°C recovers the linewidth and P donor concentration. Moreover, annealing the passivated sample at temperatures between 150 and 350°C yields additional broadening in the ESR line. These suggest that high concentration hydrogen in Si changes spin relaxation of P donor and an intermediate state is formed via dissociation of P-H complexes by annealing at 150-350°C.

In order to clarify the idea, we have investigated in detail donor-concentration and spatial distribition dependence of hydrogen passivation using P ion implantation. These results will be reported.

INTERACTION OF DEUTERIUM WITH INTERNAL SURFACES IN SILICON

S. M. MYERS, D. M. FOLLSTAEDT, H. J. STEIN, AND W. R. WAMPLER
Sandia National Laboratories, Division 1112
Albuquerque, NM 87185, USA

The strength of deuterium (D) bonding at the surfaces of closed cavities within Si was obtained from ion-beam experiments. The Si-D bond energy for low coverage corresponding to monohydride chemisorption is 2.5 ± 0.2 eV. This is believed to be the first quantitative characterization of H bonding on a Si surface, with uncertainties inherent in the interpretation of external-surface desorption being circumvented. The result is smaller than the widely assumed values above 3.0 eV, and it suggests a revised model of desorption.

Cavities were formed within Si by He ion implantation and subsequent annealing at 700°C; the cavities were localized at depths near 280 nm and had a typical size of 10 nm as observed by TEM. Deuterium was introduced by ion implantation or by heating in D_2 gas at 600°C. Infrared vibrational spectroscopy and D profiling using the nuclear reaction $D(^3He,p)^4He$ showed that the D became attached to the walls of the internal cavities by Si-D bonding. During subsequent temperature ramping, the D atoms first moved from the bound chemisorbed state into solution within the Si lattice, then diffused to the outer surface of the sample, and finally desorbed from that surface. This was observed by D profiling and IR vibrational spectroscopy, and the results were quantitatively interpreted in terms of the Si-D bond energy at the internal surface by using diffusion-trapping theory.

The present experiments complement previous studies of external-surface desorption in that they remove the complication of H-H recombination during the rate-determining step. Thus, in the case of external-surface desorption, the measured activation energy E_D is related to the Si-H bond energy E_B and the H-H recombination energy E_R by

$$2 \cdot E_B - E_R \le E_D \le 2 \cdot E_B$$

where the range reflects uncertainty over whether the highest-energy intermediate state preceding the recombination event has zero, one, or two unbonded H atoms. This uncertainty is avoided in the release from internal surfaces, since the rate-determining steps of detrapping and subsequent lattice diffusion do not involve recombination.

Our value of the Si-H bond energy, 2.5 eV, is close to the activation energies reported for desorption from external (100) and (111) surfaces. This suggests a desorption reaction path in which the rate-determining step is the breaking of one Si-H bond, followed by the exothermic reaction $H + {>}Si{-}H \rightarrow H_2 + {>}Si{-}$.

This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-AC04-76DP00789.

Measurements relating to the solubility of hydrogen in silicon at high temperatures.

S A McQuaid and R C Newman,
Interdisciplinary Research Centre for Semiconductor Materials,
The Blackett Laboratory, Imperial College,
Prince Consort Road, London SW7 2BZ, UK

E C Lightowlers
Department of Physics, Kings College,
Strand, London WC2R 2LS, UK

The formation of hydrogen-sulphur complexes in silicon that has been heated in hydrogen gas at 1300°C and then quenched has already been demonstrated [1]. The presence of hydrogen was shown unambiguously by frequency shifts in the corresponding electronic transitions when hydrogen was substituted by deuterium. However direct information about the concentration of hydrogen, [H], present in the crystal at the high temperature was not obtained.

It is well known that hydrogen also forms neutral pairs with boron acceptors leading to infrared absorption at 1904cm^{-1} (4.2K) due to the hydrogen stretching mode in the complex. The concentration of pairs, [H-B], is directly proportional to the integrated absorption, IA, of this line but to determine the concentration [H-B] it is necessary to establish a calibration. Although such calibrations have been reported for H-Al and H-Ga complexes [2] we are unaware of similar data for the H-B pair.

We have now passivated two types of boron doped silicon using a 13.56MHz hydrogen plasma. Both an MBE grown epitaxial layer and ion implanted material were completely passivated leading to indistinguishable calibrations in which a value of IA=1cm^{-2} corresponded to [H-B]=3.0×10^{15}cm^{-3}.

Boron doped Czochralski silicon samples with [B]~10^{17}cm^{-3} were then heated at various temperatures in the range 800°C to 1300°C in an atmosphere of hydrogen and quenched to room temperature. H-B pairs were detected for samples annealed at T$\geq$900°C. An Arrhenius plot of their concentration yielded the relationship:- [H-B]=5.6×10^{18}exp[-0.95eV/kT] cm^{-3}. The solubility of hydrogen at the anneal temperature, [H_s], must have been greater than [H-B], i.e., [H_s]>5.1×10^{15}cm^{-3} at 1300°C and [H_s]>4.7×10^{14}cm^{-3} at 900°C. These lower limits are comparable but somewhat greater than the values reported by van Wieringen and Warmoltz [3]. Other measurements will be reported for Float Zone silicon with a range of boron doping levels.

1. R E Peale, K Muro and A J Sievers, Materials Science Forum, Vols 65-66, p151 (1990)
2. M Stavola, S J Pearton, J Lopata and W C Dautremont-Smith, Appl. Phys. Lett., Vol. 50, p1086 (1987)
3. A van Wieringen and N Warmoltz, Physica, Vol. 22, p849 (1956)

DONOR-HYDROGEN COMPLEXES IN SILICON STUDIED BY MÖSSBAUER SPECTROSCOPY

Z.N. LIANG and L. NIESEN
Laboratorium voor Algemene Natuurkunde, MSC
Westersingel 34, 9718 CM GRONINGEN, The Netherlands

Hydrogen passivation of shallow levels in Si has been extensively studied in recent years. Great progress has been made in the understanding of hydrogen behavior in p-type Si, notably in boron doped Si. However, the knowledge on the behavior of hydrogen in n-type Si is much poorer.

We have applied Mössbauer spectroscopy to study Sb-H complexes in Si, using the 23.9 keV γ-ray transition of ^{119}Sn populated in the decay of ^{119}Sb. Various doses of 110 keV Sb ions were implanted into p-type as well as into n-type Si wafers. The samples were annealed at 900° C for 30 minutes in flowing N_2 gas, then postimplanted at room temperature with 200 eV H_2^+ (typical dose of $2x10^{15}$ H/cm^2). With this procedure the hydrogen is introduced without accompanying lattice damage. The stability of the complexes was investigated by subsequently annealing the samples at stepwise increasing temperatures and by taking the ^{119}Sn Mössbauer spectra at 80 K before and after H-implantation and after each annealing step. Sb-H complex formation as a function of hydrogen dose was studied by taking Mössbauer spectra in the hydrogen implantation set up. Furthermore, Mössbauer spectra were measured as a function of sample temperature.

In addition to a single line (IS=1.8 mm/s) associated with Sb(Sn) atoms at the substitutional sites, we have observed a line with IS=2.3 mm/s after the introduction of hydrogen, which is due to the formation of an Sb-H complex. This Sb-H line shows a Debye temperature close to that of the substitutional line, and disappears upon annealing at 520 K. The isomer shift of this line is practically independent of Sb and H doses. However its linewidth increases sharply below a dose of 10^{13} Sb/cm^2. The results can be understood by assuming that these two types of Sb-H lines are associated with trapping of H^0 and H^- by ionized donors, resulting in different geometries for the Sb-H complexes. In other words, the formation of these Sb-H complexes depends on the local Fermi level. Surprisingly, the total intensity of the spectra decreases as the intensity of the Sb-H lines increases. This strongly indicates that there exist some other complexes which have such low recoilless fractions that they are not visible even at 20 K. Further experiments are required to understand this very strange behavior.

HYDROGEN-ASSISTED THERMAL DONOR DEPTH PROFILES

H. J. STEIN, S. K. HAHN*, AND P. M. RICHARDS
Sandia National Laboratories, Division 1112
Albuquerque, NM 87185, USA
* Dept. of Matls. Sci. and Eng., Stanford University
Stanford, CA 94305, USA

We have previously shown that a hydrogen plasma enhances the thermal donor (TD) formation rate in Czochralski Si by an order of magnitude at 400°C. The infrared absorption signatures for the excited states of the resultant donors are the same as those for TD's formed at a lower rate without the hydrogen assist. As an approach to determine mechanisms involved in hydrogen-assisted TD formation, we have used spreading resistance probe (SRP) measurements to investigate the depth profiles for hydrogen-assisted TD formation as a function of time and temperature between 350 and 400°C. Infrared (IR) absorption has been used to verify the nature of the TD's which are formed in the hydrogen plasma. Our results on penetration depths for hydrogen-assisted TD formation show: 1) a square root of time dependence for the depth, 2) a temperature dependence for the depth, 3) a nearly constant donor concentration in the assisted depth range for a given exposure, followed by a sharp decrease at the end of the penetration depth, and 4) an increase in donor concentration in the assisted depth with time and temperature. The findings indicate the complexity of the hydrogen-assisted process, and modeling has been undertaken to aid interpretations. The square root of time dependence for the penetration depth is in accord with a diffusion-limited process, and, indeed, the actual depth from a given exposure is approximately what would be expected for atomic hydrogen diffusion in Si. However, the temperature dependence for the penetration depth range gives an activation energy of 1.5 ± 0.2 eV, rather than the value of 0.5 eV generally accepted for hydrogen diffusion in Si. The anomalously high activation energy can possibly be explained by a thermally-activated release of hydrogen into the bulk from traps near the surface where hydrogen ions impinge during plasma exposure. Additional experiments and modeling are continuing in an effort to understand the shape of the profile, and the time and temperature dependence of the donor concentration in the hydrogen-assisted-formation depth.

This work was supported in part by the U.S. Department of Energy under contract number DE-AC04-76DP00789.

PASSIVATION OF SHALLOW ACCEPTORS IN Si AND GaAs BY ANNEALING IN H_2

I.A. VELOARISOA, D.M. KOZUCH, M. STAVOLA, R.E. PEALE, and G.D. WATKINS, Physics Department, Lehigh University, Bethlehem, PA 18015

and

S.J. PEARTON, C.R. ABERNATHY, and W.S. HOBSON, AT&T Bell Laboratories, Murray Hill, NJ 07974

Most recent studies of the intentional passivation of shallow impurities have focussed on the indiffusion of H from an H-containing plasma. There are a number of cases in which shallow impurities can be effectively passivated by annealing samples in H_2 gas. We have found that shallow acceptors in Si can be passivated throughout the bulk of a sample that is several mm thick by annealing in H_2 at 1250°C and quenching [1]. We have also found that epitaxial layers of heavily C-doped GaAs can be passivated by annealing in H_2 near 500°C and quenching [2]. In this paper we describe infrared absorption and electrical measurements that confirm the passivation of shallow impurities in Si and GaAs that have been annealed in H_2. The free hole concentrations are decreased in samples annealed in H_2 and infrared absorption features that have been previously assigned to B-H, Ga-H, and Al-H complexes in Si and the C-H complex in GaAs are observed. The effect of H_2 in growth and annealing ambients on the concentration of shallow acceptors will be discussed.

1. I.A. Veloarisoa et al., Bull. Am. Phys. Soc. 36, 945 (1991).

2. D.M. Kozuch, M. Stavola, S.J. Pearton, C.R. Abernathy, and W.S. Hobson, to be published.

The portion of this work done at Lehigh University was supported by U.S. Office of Naval Research Grant No. N00014-90-J-1264.

Session PL

Metal Impurities in Elemental Semiconductors

Wednesday Evening, 24 July

Rathbone Hall

Nickel related Deep Levels in Germanium

F.X. Zach, H. Grimmeiss[1], E.E. Haller

Lawrence Berkeley Laboratory and University of California at Berkeley, Berkeley, CA 94720, USA

1) Permanent address: Department of Solid State Physics, University of Lund, Box 118, S-221 00 Lund, Sweden

We have studied Ni related deep levels in vacuum and hydrogen atmosphere grown Ge single crystals using deep level transient spectroscopy. For the first time, not only the emission rates, but also the capture constants as a function of temperature were determined for these levels. We present additional data on commonly observed, interfering traps that are found in Ge crystals.

Ni was introduced into Ge by diffusion of Ni coated crystals. The capacitance transient of reverse biased diodes following short (0.1 - 1000 μs) pulses were recorded using a Miller correlator or a digital storage oscilloscope. In addition we performed steady state photocurrent measurements on the short circuited diodes.

Substitutional Ni is assumed to act as a double acceptor in Ge, however conflicting results on the position of the energy levels are found in the literature[1,2]. We reexamined the case of Ni related centers in Ge and studied the temperature dependence of the emission rates and capture constants for Ni related levels. Our data enable us to determine, for the first time, the exact position of the energy levels within the bandgap: The activation energies of the emission rates obtained from the Arrhenius plots have been corrected for the temperature dependence of the capture constants. Using these data we were able to calculate the Gibb's free energy as a function of temperature for each of the centers studied. Further analysis provided data on the overall entropy change of the carrier emission process. The Ni related levels were studied in crystals grown under various conditions. We present data obtained for crystals that contain hydrogen, as hydrogen is known to form complexes with numerous defects and impurities. In particular hydrogen leads to partial passivation of multivalent acceptors such as Cu[3] and possibly Ni as well.

The photocurrent measurements yield complementary information on the position of the energy levels.

1) Milnes, A.G. : Deep Impurities in Semiconductors, Wiley and Sons, New York 1973

2) Pearton, S.J.,:Solid State Electronics 25(1982) p. 305

3) J.M. Kahn, L.M. Falicov, E.E. Haller : Physical Review Letters 57(1986) p. 2077

ELECTRONIC NATURE OF NEUTRAL ZINC IN SILICON: FTIR-ABSORPTION, UNIAXIAL STRESS MEASUREMENTS

B. KAUFMANN, A. DÖRNEN, M. LANG*, G. PENSL*
D. GRÜNEBAUM‡, and N. STOLWJIK‡
4. Physikalisches Institut, Universität Stuttgart, F.R.G.
*Institut für Angewandte Physik, Universität Erlangen, F.R.G.
‡Institut für Metallforschung, Universität Münster, F.R.G

An Effective-Mass(EM)-like spectrum, recently observed in infrared spectroscopy at around 320 meV in zinc diffused silicon was related to the isolated zinc double acceptor [1,2].

In this paper we present absorption measurements on these bound- to-bound transitions focusing on the electronic nature of neutral zinc. From temperature-dependent measurements we get evidence that the EM-like excited states are also split into three sublevels as already found for the ground state. For the excited states we find a splitting which is about one third of the spacings in the ground state. In a previous paper we followed the discussion on double acceptors in germanium and tried to explain the ground state to be made up by both the j-j coupling of the two bound holes and the additional crystal-field splitting of the tetrahedral surrounding [1]. But the relatively large splitting in the EM-states found now, suggests j-j-coupling not to be the dominant interaction in neutral zinc.

This view is supported by measurements under uniaxial stress, carried out for the $<100>$, $<111>$ and $<110>$ stress direction. We find a splitting pattern which is highly anisotropic, showing the strongest stress response for the $<100>$ stress direction. The most prominent line of the zinc spectrum (I_2) splits into four components, strictly proportional in stress. Instead of a j-j-coupling model, the anisotropic stress behavior found here, suggests a dominant $<100>$ -axial character of the center, possibly caused by a (dynamic) Jahn-Teller-Effect. The observed thermalization among the stress induced lines is in accordance with this model, too.

We will discuss our results in terms of a possible Jahn-Teller distortion and compare our data with the double acceptor copper in GaAs where a similar mechanism is believed to be observed.

[1] A.Dörnen, R.Kienle, K.Thonke, P.Stolz, G.Pensl, D.Grünebaum, and N. Stolwijk, Phys. Rev. B 40, 12005 (1989)
[2] E.Merk, J.Heyman, and E.E.Haller, Solid State Commun., 72, 851 (1989)

Vibronic Interaction at a Gold-Related Center in Silicon.

S Ghatnekar, M Kleverman, and H G Grimmeiss
Department of Solid State Physics, University of Lund
Box 118, S-221 00 LUND, Sweden

Only a few examples of deep levels in silicon showing vibronic effects have sofar been reported. In this paper, clear evidence for a vibronic interaction at a gold-related center in silicon will be presented and discussed in detail. The new line spectrum has been investigated by means of transmission spectroscopy using uniaxial stress. The spectrum consists of a prominent zero-phonon line at 6120 cm^{-1}, followed by several phonon replicas. The replicas are split into two, three, and four components for the one, two, and three phonon replicas, respectively, with a phonon energy of about 57.4 cm^{-1}. The number of components is typical for a weak Jahn-Teller (JT) interaction of $E \otimes E$ type. This identification is further supported by the close agreement between the experimentally observed and the calculated splittings in terms of the coupling strength. The JT interaction is considerably stronger in the initial state of the transitions and its strength can be estimated from calculations of the relative intensities of the lines in the spectrum.

Doping and thermal annealing experiments suggest the defect to be a complex involving two substitutional gold atoms and an iron atom on tetrahedral interstitial site.

The defect has been studied by uniaxial stress and Zeeman spectroscopy which will be presented and discussed in detail.

The Gold Center in Silicon

A Thilderkvist, G D Watkins*, M Kleverman, and H G Grimmeiss
Department of Solid State Physics, University of Lund
Box 118, S-221 00 LUND, Sweden

The electronic structure of the well known substitutional gold center in silicon has over the years been disputed. An important aspect has been the inability to observe any EPR signal. Here we report on Zeeman and uniaxial stress studies of the donor and acceptor excitation spectra at 793 meV and 611 meV, respectively. The results give clear evidence for a <100>-tetragonal distortion for the neutral center, which is paramagnetic, S=1/2, with $g_{||} \approx 2.8$ and $g_{\perp} \approx 0$. Reorientation effects are observed which occur even at 1.9K, as evidenced by thermalization of the corresponding Zeeman-split components. The Au center behaves similarly therefore to the isoelectronic Pt^- defect (S=1/2, $g_{||} \approx 2.1$, $g_{\perp} \approx 1.4$) which from EPR studies has been established also to have a static tetragonal distortion with reorientation at these temperatures. It differs in two important respects, however, in that a considerably orbital contribution has to be attributed to $g_{||}$ and that $g_{\perp}$ is close to zero. A recent explanation given by Anderson[1] accounts for the inability to detect the Au center by EPR. In his model, $g_{\perp}=0$ could result either from rapid tunneling between the two equivalent configurations of a superposed off-center C_{2v} distortion (observed as static for Pt^-) or by an increased spin-orbit interaction which quenches the distortion. The increased orbital contribution to $g_{||}$ suggests the latter.

1 F G Anderson, APS March Meeting 1991.

* Permanent address: Physics Department, Building 16, Lehigh University, Bethlehem, PA 18015, USA

ELECTRONIC STATES OF Mn_4 AND Fe_4 CLUSTERS IN SILICON

José R. LEITE, Lucy V.C. ASSALI, and Antônio T. LINO
Instituto de Física da Universidade de São Paulo,
C.P. 20516, São Paulo, 01498, S.P., Brazil

It is known from pioneering EPR experiments that when Si samples containing only Mn impurities are cooled slowly from elevated temperatures a dominant paramagnetic center composed of four Mn atoms is formed. The complex gives rise to a spectrum displaying 21 hyperfine lines with a fine structure characteristic of S=2 and J=0 values. The symmetry of the spectrum shows that the four Mn atoms are equivalent and arranged in a tetrahedron, probably at the nearest interstitial sites. Recently the Mn_4 cluster was also identified by EPR in high resistivity p-type and n-type Si doped with Mn. However, a total spin S=6 was ascribed to the complex. Besides the discrepancies concerned to the EPR data, the reported positions of the energy levels induced by the complex in the Si band gap are also quite controversial.

It has been also shown from recent EPR measurements that the annealing of Fe-doped high-resistivity Si samples yields a S=4 spectrum which can be ascribed to a complex consisting of four interstitial Fe atoms. The Mn_4 and Fe_4 clusters are very good prototypes to study the interaction mechanisms between transition metal impurities in Si. Nevertheless, very little is known about their microscopic and electronic structures.

In this work we have carried out, for the first time, SCF spin-polarized one-electron state calculations for the Fe_4 and Mn_4 complexes in Si. The results were obtained by using a molecular cluster model and the multiple-scattering $X\alpha$ theory. It has been found that Fe_4 is a high spin complex (S=4) in agreement with EPR experiments. However, the calculations indicate that the ground state of the Mn_4 cluster is non paramagnetic. Excited states of this center have been simulated in order to interpret the EPR results.

One important conclusion which emerges from the calculations is that the magnetic properties of the clusters can not be inferred directly from the magnetic properties of the isolated impurities. The total spin of the complex does not arise from the coupling between the localized spins of four magnetic centers, as has been currently assumed, but is rather related to the 3d-derived molecular orbitals of the complex which are spread out over the entire cluster.

Copper neutralization of acceptors and related defects in p-type silicon

A.Mesli and T. Heiser
Laboratoire PHASE (UPR du CNRS n°292), 23 rue du Loess, 67037 Strasbourg Cedex, France

Copper diffused and fast quenched p-type silicon crystals exhibit two main effects. Uniform neutralization of acceptors through the whole material and creation of copper related defects. As already reported, acceptor neutralization corresponds to pairing reactions between the acceptor atom and the so called fast diffusing X species. It is shown in this work that the gallium-X defect is more stable than the boron-X complexe. However, both can be completely dissociated under high electric fields well below room temperature.

Following this procedure, DLTS measurements reveal two deep levels. A shallow level located at 0.1eV above the valence band and attributed to the Cu-Cu pair thermally stable up to 150°C and a deeper level located at E_V+ 0.21eV. If the structure of this last defect remains unknown, we show that neither acceptor (B, Al, Ga) nor oxygen are involved in its formation. However, it exhibits the electronically induced metastability. Two different mechanisms could lead to such behavior. Classical configurational bistability or reversible pairing reactions involving the fast diffusing X defect.

In this work, we identify the process governing such metastability by properly controlling the Fermi level effect. The barriere energies and the transformation rates are extracted from the kinetics and a modele is proposed.

DIFFUSIVITIES OF 3D TRANSITION-METAL IMPURITIES IN SILICON

H. NAKASHIMA* and K. HASHIMOTO**

* *Department of Electrical Engineering, Kyushu University, Fukuoka 812, Japan*

** *Department of Physics, Kurume Institute of Technology, Fukuoka 830, Japan*

Properties of 3d transition-metal impurities in Si have been studied for the last 30 years and reviewed in detail in the paper by Weber. All 3d elements are believed to migrate owing to a simple interstitial diffusion mechanism, and diffusivities of the 3d elements have been rather well established as shown in the recent paper by Utzig. However, there is no experimental data available for V. In addition, some of the diffusivities have been determined in the narrow 1/T interval. In order to obtain more reliable migration enthalpies, it is necessary to determine the diffusivity in the more expanded 1/T scale.

In the present study, diffusivities of Ti, V, Mn and Fe in Si have been investigated in three different temperature range. In the high temperature range (900-1200℃) an in-depth profile measurement by deep level transient spectroscopy (DLTS) was used for Ti, V and Fe, and in the lower temperature range (600-800℃) an annealing experiment which employed a technique for profiling the concentration of deep level within a depletion region was used for Ti and V. The obtained profiles are well described by the solution of Fick's equation, and the fit yields the diffusivity for each element. In the room temperature range (0-90℃) the diffusivities for Mn and Fe are studied by monitoring the pairing reaction of these elements and substitutional B.

From these measurements based on DLTS, the diffusivity D of each element is obtained as follows:

$$D_{Ti} = 1.1\times10^{-1}\exp(-2.05/kT)\ \mathrm{cm^2 s^{-1}} \quad 600\le T\le 1150℃,$$

$$D_{V} = 9.0\times10^{-3}\exp(-1.55/kT)\ \mathrm{cm^2 s^{-1}} \quad 600\le T\le 1200℃,$$

$$D_{Mn} = 2.4\times10^{-3}\exp(-0.72/kT)\ \mathrm{cm^2 s^{-1}} \quad 14\le T\le 90℃,$$

$$D_{Fe} = 1.1\times10^{-3}\exp(-0.66/kT)\ \mathrm{cm^2 s^{-1}} \quad 0\le T\le 1100℃.$$

By comparing these results with published data, the diffusivities of 3d transition-metal impurities in Si are discussed.

$\langle 100 \rangle$ AND $\langle 111 \rangle$ CONFIGURATIONS OF IRON-ACCEPTOR PAIRS IN SILICON RELATED TO STABLE AND METASTABLE STATES

Hideki TAKAHASHI, Masashi SUEZAWA and Koji SUMINO
Institute for Materials Research, Tohoku University, Sendai 980, Japan

Two structural configurations, one with $<111>$ trigonal and the other with $<100>$ orthorhombic symmetry, have been revealed by means of ESR technique for a pair of iron impurity and dopant acceptor, such as Fe-Al, Fe-Ga and Fe-In pairs, in Si. On the other hand, DLTS studies have found that there are stable and metastable states of such Fe-acceptor pairs. This paper clarifies the relation between the two structural configurations and their stability from the determination of energetic parameters related to the two structural configuration by means of ESR technique.

Si crystals doped with Al or Ga grown by the floating-zone-technique were doped with Fe impurity by annealing at 1300℃ together with Fe pieces followed by rapid quenching. Specimens were kept at liquid nitrogen temperature until they were subjected to ESR measurements with an X-band spectrometer at 10 K.

Isochronal annealing of a quenched specimen starting from 40℃ has revealed that the concentrations of both Fe-Al and Fe-Ga pairs first increase, attain the maxima at about 100℃, and then diminish with increasing temperature. Contrarily, the concentrations of both electrically neutral iron Fe^0 and positively charged iron Fe^+ decrease with temperature and attain the minima at about 100℃. They increase on further increase in the temperature, showing maxima at 150℃, and then diminish. The whole process is described with the pairing and depairing of Fe and acceptor atoms in the temperature range 40 – 150℃ and precipitation of Fe at higher temperatures.

From the analysis of the generation processes of the $<111>$ and $<100>$ pairs it is concluded that the $<111>$ pair is the stable state and the $<100>$ pair the metastable state of both Fe-Al and Fe-Ga pairs. The differences in the configurational energy between the $<100>$ and $<111>$ pairs have been determined to be 0.07 ± 0.01 and 0.03 ± 0.01 eV for Fe-Al and Fe-Ga pairs, respectively. These values are in good agreement with the energy differences of the stable and metastable states of Fe-Al and Fe-Ga pairs as determined with DLTS.

The analysis of the experimental data of this work has further led to the conclusion that the activation energies for the migration of Fe^0 and Fe^+ in Si to be 0.80 ± 0.01 and 0.68 ± 0.01 eV, respectively.

Interaction between copper and irradiation-induced defects in crystalline silicon

B.G. Svensson
Royal Institute of Technology, Solid State Electronics
P.O. Box 1298, S-164 28 Kista-Stockholm, Sweden

M.O. Aboelfotoh
IBM Research Division, T.J. Watson Research Center
P.O. Box 218, Yorktown Heights, N.Y. 10598, USA

Schottky barrier (SB) structures of the type Cu/Si(100) have been formed by the deposition of copper on both n- and p-type silicon substrates. Prior to the deposition the substrates were irradiated by 2 MeV electrons at nominal room temperature to doses in the 10^{15}-10^{17} cm^{-2} range. The SB structures were characterized by capacitance-voltage (CV) measurements, deep level transient spectroscopy (DLTS) and optical techniques (infrared spectroscopy and photoluminiscence).

In the n-type samples an anomalously high annealing rate of the divacancy (V_2) acceptor levels is observed below ~150 °C, and fast diffusing interstitial Cu^+ is believed to passivate the electrical activity of the V_2 centers by formation of neutral complexes. In the temperature range 150-200 °C, where the metal-rich silicide η'-Cu_3Si forms, the concentration of V_2 stays almost constant and, no rapid annihilation takes place, i.e., we find no evidence for the injection of silicon self-interstitials during the growth of η'-Cu_3Si (in contrast to recent experiments reported in the literature).

In the p-type samples a Cu-associated level appears ~0.53 eV above the valence band (E_v) directly after deposition. Profile measurements of this level reveal a constant concentration over depths larger than 4 μm and indicate a substantial diffusion of Cu into the silicon substrate at room temperature. The level anneals out below ~150 °C, and simultaneously a considerable decrease in the concentration of the two levels at E_v+0.25 eV (transition between the neutral and positive charge state of V_2) and E_v+0.35 eV (carbon oxygen center) takes place.

On the basis of these results, the interaction of Cu with irradiation-induced defects is discussed, and in particular, evidence for copper passivation of vacancy type defects involving broken bonds is presented. Moreover, point defect generation during silicide formation is considered, and we show that the type of point defect injected into silicon is generally not determined by the dominant moving species during silicidation.

Interaction of a Copper-Induced Defect With Shallow Acceptors and Deep Centers in Silicon

Th. Prescha and J. Weber
Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 7000 Stuttgart 80, Federal Republic of Germany

It is well established that copper introduces in silicon the fast diffusing X-defect.[1] We will report on the properties of complexes formed by the X-defect with shallow acceptors or deep centers.

In p-type Si the X-defect forms electrically inactive complexes (AX) with the acceptors (A). Capacitance voltage (CV) measurements on Schottky diodes provide the profile of the electrically active acceptors and allow us to study the thermal dissociation of the AX complexes. In the space charge region of a Schottky diode the electric field drifts the X-defect like a positively charged species into the bulk of the semiconductor. The dissociation process of the AX-complexes in the space charge region shows first order kinetics with different dissociation energies in the range $E_d = 0.6 - 0.7eV$ for the acceptors A = B, Al, Ga and In.

The X-defect interacts also with deep defects (Pt, Pd and Au) in Si. A detailed investigation is presented for the PtX complex. Platinum doped samples reveal after introducing copper a new defect level at $E_a = 560meV$. Annealing the samples under reverse bias reduces the concentration of the new defect and a defect level at $E_a = 320meV$ appears. The total concentration of both levels remains constant under annealing below T=300K with or without reverse bias applied.

Although the annealing seems to demonstrate a metastable behavior of the new complex, a more careful investigation of the concentration profiles unambiguously supports a different process. The new defect complex is formed between the Pt donor and the X-defect. The PtX complex dissociates under the annealing conditions and activates the Pt donor at $E_a = 320meV$. The X defect drifts due to the electrical field towards the end of the space charge region.

[1] Th. Prescha, T. Zundel, J. Weber, H. Prigge and P. Gerlach, Materials Science and Engineering, **B4**, 79, (1989).

UNIAXIAL STRESS ALIGNMENT STUDIES OF Pd^- AND Ni^-

P.M. WILLIAMS, F.S. HAM, F.G. ANDERSON, and G.D. WATKINS
Physics Department and Sherman Fairchild Laboratory,
Lehigh University, Bethlehem, PA 18015

We report the results of uniaxial stress alignment studies on the isolated substitutional Pd^- and Ni^- defects in silicon. We find that these defects reorient under stress in the same sense as the Pt^- defect in silicon. From these results we may infer the ordering of the Jahn-Teller split t_2 states in the band gap. This information is essential in modeling the electronic structure of these defects.

As shown by electron paramagnetic resonance (EPR), each of these centers possesses C_{2v} symmetry. The application of uniaxial stress removes the orentational degeneracy of the six equivalent orientations. By observing the change versus stress of the relative EPR intensities for differently oriented defects, we determine the elements of the piezospectroscopic tensor (B) giving the energy shift of each orientation as a function of strain.

The defect principal axes for these defects is identical to that of the negatively charged silicon vacancy (V^-). In the defect principal axis system, B is diagonal and has components $B_x= 0.13$, $B_y=-4.71$, and $B_z= 4.58$ eV/unit strain for the Pd^- defect and $B_x=-0.53$, $B_y=-2.42$, and $B_z= 2.95$ eV/unit strain for the Ni^- defect. As in the case of the Pt^- defect, the values of B_x-B_y and B_z for each defect have the opposite sign to those values for V^-.

The electronic structures of each of the Pt^-, Pd^-, and Ni^- defects is described by the "vacancy model." This model is characterized by the presence of a triply occupied t_2 level in the bandgap that is only weakly localized on the impurity atom. The orbital degeneracy of this level is entirely lifted by combined tetragonal and trigonal Jahn-Teller (JT) distortions. For the special case of three electrons, the vacancy model does not predict the final ordering of the JT split t_2 states.

From our results, we conclude that the ordering of the JT split t_2 states for Pd^- and Ni^- is the same as for the Pt^- case, i.e., inverted from the ordering of the states for the case of V^-. This might be a surprising result in light of the fact that the g values measured by EPR in going from Pt^- to Ni^- become more like those found for V^-. Finally, as in the case of Pt^-, we observe the Pd^- and Ni^- defects to reorient even at 4.2K, suggesting that the barrier for reorientation is quite small, and that these defects possess a strong vibronic character.

This research has been supported by the U.S. Navy Office of Naval Research Contract No. N00014-90-J-1264.

Shallow Excited States of the 1014 meV Cu-related Optical Center in Silicon. M.H.Nazaré, A.J.Duarte, Departamento de Física, Universidade de Aveiro, 3800 Aveiro, Portugal; and A.Steele, G.Davies E.C.Lightowlers, Department of Physics, King's College London, Strand, London WC2R 2LS, UK.

Transition metals diffuse very rapidly into crystalline silicon, producing many photoluminescence bands, the vast majority of which has been interpreted as radiative recombination of excitons bound at the isoelectronic impurity. The most relevant examples are the 1014 meV and 943 meV Cu-related bands and the 1067 meV and 735 meV Fe-related bands.

These bands have multiple excited states with similar energy separations. The response to external applied fields of these states and a critical comparison of the results obtained for each center can provide valuable information on the stabilization mechanism of the TM related defects.

Here we report the behaviour, under uniaxial stress, of the excited states at 1016 meV and 1024 meV of the copper center whose main line occurs at 1014 meV. Data is reported and quantitatively analysed, yielding the stress parameters for the three lines. These results are compared with ones reported for the other copper center at 943 meV.

Session PM

Oxygen in Semiconductors

Wednesday Evening, 24 July

Rathbone Hall

MORPHOLOGY CHANGE OF OXYGEN PRECIPITATES IN CZ–SI WAFERS DURING TWO–STEP HEAT TREATMENT

Masami Hasebe and James W. Corbett

The Institute for the Study of Defects in Solids
Department of Physics
The State University of New York at Albany
Albany, NY 12222, USA

Kazuto Kawakami

Electronics Research Laboratories
Nippon Steel Corporation
1618 Ida, Nakahara, Kawasaki, Kanagawa 211, Japan

We have studied the morphology change of oxygen precipitates and the formation of the secondary defects, such as stacking faults and dislocation loops, during two-step annealing in CZ-Si wafers by TEM observation and solute-oxygen concentration measurement by FTIR.

We have found that the morphology change of the precipitates between low and high temperature heat-treatments is not continuous; thermal donors dissolve into solute oxygen, and low temperature precipitates (platelets) shrink and dissolve and simultaneously newly formed precipitates (octahedra) are nucleated in the second high temperature annealing. As the secondary defects of the precipitation, dislocation loops are dominant in the first low-temperature annealing in association with the platelet formation; however, stacking faults are mainly remaining after the octahedron formation.

We will discuss the formation mechanism of the precipitates from the view point of the morphology and structure change between low and high temperature annealing, and we will propose that (1) thermal donors are not to become the nuclei of the higher temperature precipitates, (2) platelet precipitates dissolve and the morphology changes to an octahedron with stacking-fault formation during the second high-temperature annealing; therefore, self-interstitial emission is strongly related to the octahedral precipitate growth but not to the platelet precipitates, and (3) the morphology of the precipitates is determined by the lattice stress/relaxation process, e.g., the forms of platelet and octahedron are related to lattice deformation and self-interstitial emission, respectively.

SILICON THERMAL DONORS: PHOTOLUMINESCENCE AND MAGNETIC RESONANCE INVESTIGATIONS OF BORON AND ALUMINUM DOPED SILICON

B. HEIJMINK LIESERT, T. GREGORKIEWICZ, and C.A.J. AMMERLAAN
Natuurkundig Laboratorium der Universiteit van Amsterdam
Valckenierstraat 65, NL-1018 XE Amsterdam, The Netherlands.

Silicon thermal donors (TD's) continue to be one of the most puzzling issues of the defect physics of silicon. In spite of concerted effort by both experimental and theoretical physics no consensus could be reached neither on the core structure of this evidently extended defect nor on the growth-development mechanism responsible for its multispecies character. Nevertheless a vast amount of evidence has been gathered and several aspects of TD centers and related phenomena could be clarified. The fingerprints of TD centers were identified by most of the experimental techniques applied in semiconductor material science. Among those the most direct information was provided by the infrared absorption spectroscopy where two TD-related ionisation series were identified. Further confirmation of the multispecies character of TD's was obtained from the EPR/ENDOR studies where two spectra namely Si-NL8 and Si-NL10 were found to be TD related, and also, more recently, from the photoluminescence spectroscopy as the luminescence lines originating from the TD-bound excitons BE have been identified.

In the present study the TD generation kinetics, as visualized by TD BE PL, have been followed for boron and aluminum doped Czochralski-grown silicon. The results were compared with the kinetics obtained for the same material from magnetic resonance studies. Further, the generation of TD related recombination PL has been studied upon IR illumination of the sample. In this case the dependence of the excitation wavelength has been followed and compared with the results of the photo-EPR experiments on the same material.

Taken together the results of our PL studies provide powerful evidence for the identification of the TD-related EPR spectra with different charge states of thermal donor center.

DEFECT DISTRIBUTION IN LARGE CZ-SILICON WAFERS INVESTIGATED BY POSITRON ANNIHILATION SPECTROSCOPY

P. MASCHER[1], W. PUFF[2], S. HAHN[3], K.H. CHO[4], and B.Y. LEE[4]

[1]Centre for Electrophotonic Materials and Devices, Department of Engineering Physics, McMaster University, Hamilton, Ontario, Canada
[2]Institut für Kernphysik, Technical University Graz, Austria
[3]Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, U.S.A.
[4]Lucky Advanced Materials Inc., #283 Imsoodong, Gumi Kyungsangbukdo, Korea

In this paper we report results of the first systematic investigation of defect characteristics across six-inch CZ-Silicon wafers using positron annihilation spectroscopy. The study was triggered by recent results [1-3] which have shown that positrons can give unique information on defects involved in oxygen precipitation phenomena in CZ-Silicon.

The wafers investigated were taken from a range of locations along the ingots (seed to tail). Ingots grown at standard and fast pull speeds were used with higher pull speeds typically resulting in lower overall interstitial oxygen concentrations. In an effort to closely correlate the positron response to oxygen precipitation phenomena radial resistivity gradients as well as radial gradients of the interstitial oxygen contents were determined for each wafer. The radial measurements were taken at 14 positions across the wafers to coincide with the positions of the measurements of the annihilation parameters. Typical resistivities ranged from 6 to 9 Ωcm (p-type) and typical interstitial oxygen concentrations, $[O_I]$ were in a range from 11 to 16 ppma.

The positron experiments utilized both lifetime and Doppler broadening techniques in order to obtain detailed information on possible vacancy-impurity interactions [3]. A first series of measurements on as-grown wafers clearly showed that the material was much more homogeneous than previously investigated samples [4] with annihilation characteristics typically stemming from small oxygen agglomerates and the "perfect" bulk material only. At the present time a new series of measurements is in progress to monitor the change of the defect profiles caused by conventional industrial post-growth heat treatment. The results will be discussed in the light of the observed oxygen precipitation characteristics.

References

[1] W. Puff and S. Dannefaer, Materials Science Forum 65-66, 307 (1990).
[2] S. Hahn, F.A. Ponce, S. Dannefaer, P. Mascher, D. Kerr, W. Puff, V. Stojanoff, S. Ishigami, and W.A. Tiller, Extended Abstract, ECS-Meeting, Montreal, Canada, May 1990.
[3] S. Dannefaer, W. Puff, P. Mascher, and D. Kerr, J. Appl. Phys. 66, 3526 (1989).
[4] S. Dannefaer and D. Kerr, J. Appl. Phys. 60, 1313 (1986).

Infrared Absorption by Interstitial Oxygen in Germanium-Doped Silicon Crystal

H. Yamada-Kaneta, C. Kaneta,* and T. Ogawa

Basic Process Development Division, Fujitsu Limited,
1015 Kamikodanaka, Nakahara-ku, Kawasaki 211, Japan
**Semiconductor Devices Laboratory, Fujitsu Laboratories Limited,*
10–1 Morinosato-Wakamiya, Atsugi 243–01, Japan

The bond-interstitial oxygen (O_i) causes, at 4.2 K, the absorptions at 1136.4 and 29.2 cm^{-1} by its bond-parallel local vibration and the bond-perpendicular anharmonic excitation, respectively.[1,2] The coupling between these two excitations further causes the absorption peak at 1205.6 cm^{-1} as the anharmonic-excitation-sideband of the local vibration transition.[1,2] The multi-peak structure in the 1100 cm^{-1} hot-band is also due to the coupling.[1] We measured the spectral variation of these absorptions caused by Ge-doping up to 13000 ppm, and investigated how this coupled excitation is perturbed.

Our experimental findings are as follows: Besides the isolated O_i (O_i-I), there are two types of O_i (Si-O-Si unit) located close to the Ge atom (O_i-II and -III). In case of 13000 ppm doping, for instance, O_i-I causes, at 4.2 K, the absorptions at 30.1, 1136.0, 1206.4 cm^{-1}, O_i-II at 32, 1130, 1209 cm^{-1} and O_i-III at 36, 1118.5 cm^{-1}. Intensity contribution per one O_i atom for these absorptions in the 30 and 1100 cm^{-1} regions remains unchanged from that of the normal O_i. (We refer to the O_i in the undoped crystal as the normal O_i.) However, the contribution to the 1200 cm^{-1} absorptions is considerably reduced: 85, 20 and $\sim$ 0 % of the normal O_i, for O_i-I, -II, and -III respectively, in case of 13000 ppm doping. Temperature dependence of the absorptions due to O_i-I, -II, and -III is similar to that of the normal O_i. However, the peak separations in the 1100 cm^{-1} hot-bands of O_i-II and -II are 50 – 30 % of the normal O_i.

Modification of the parameter values in the Hamiltonian[1] for the normal O_i gave the energy levels for O_i-I, -II, and -III which well explain the observed peak energies. The coupling and the bond-perpendicular anharmonicity (off-center nature) of O_i-II and -III were much weaker than those of the normal O_i. The eigenfunctions for O_i-I, -II, and -III described satisfactorily the intensity reduction observed for the 1200 cm^{-1} absorptions. The dominant factor for it is the weakening of the coupling and anharmonicity, to which the probability of the 1200 cm^{-1} transitions is much more sensitive than that of the 30 and 1100 cm^{-1} transitions. The sensitivity originates from the sideband nature of the 1200 cm^{-1} transitions.

1) H. Yamada-Kaneta, C. Kaneta, and T. Ogawa. Phys. Rev. B 15, 9650 (1990).

2) D. R. Bosomworth, W. Hayes, A. R. L. Spray, and G. D. Watkins, Proc. R. Soc. London Ser. A 317, 133 (1970).

NEW EVIDENCES FOR THE DEFECT MODEL OF PHOTOCONVERSION BY OXYGEN IN GaAs

Xue-Fu Zhong
The institute of semiconductors, Chinese academy of sciences

Some new experiments, including piezospectroscopic study[1] and electronic energy level measurements[2] on the oxygen defect of photoconversion in GaAs, are analyzed on the basis of the defect model suggested by author and coworkers[3,4] The analysis indicates that the results are in good agreement with the prediction by the model.

The piezospectroscopic measurement demonstrates that the dipole moment of Ga-O bond is along (110) direction. The model calculation, taking the lattice relaxation into account, provides the bond length of Ga-O bond is close to one half of the distance between two Ga atoms at equilibrium. So the three atoms in the defect center are embedded in a plane which is parallel to x-z plane. The measurement and the calculation both confirm the spatial structure of the defect center.

The measurements on electronic energy levels gave the results that the electronic state in the gap corresponding to $Ga\text{-}O^{-2}$ bond is lower than that to $Ga\text{-}O^{-1}$ bond. So the defect seems to behave like a negative U (negative affinity) center. Our model analysis assumes that these energy levels in the gap are due to unbonded electrons on oxygen atom. Their orbital energies are much affected by the charge state of the atom. Since the charge transfer is opposite for the $Ga\text{-}O^{-1}$ and $Ga\text{-}O^{-2}$ bonds, the changes in orbital energy of unbonded electrons are different for these two cases. A quantitative estimate by self-consistent bond orbital model leads to the energy difference which is close to the observation. The model calculation clarifys the influence on cohesive energy of the cluster by these unbonded electrons and explains why the charge state of O^{-2} is more stable than O^{-1} state. This may be taken as a new mechanism for negative U center.

* Work supported by the National Foundation of Natural Sciences.

1. Song et al., Phys.Rev.,B41,12330,1990.
2. M.Skowronski et al.,Appl.Phys.Lett.,57,902,1990.
3. X.F.Zhong et al.,Appl.Phys.Lett.,52,628,1988.
4. X.F.Zhong et al.,J.Appl.Phys.,69,1124,1991.

Session PN

Defects in Compound Semiconductors

Wednesday Evening, 24 July

Rathbone Hall

Combined Study of Complex Defects in Semiconductors

P.L. Souza*, C.W. Rodrigues† and M.J. Caldas†

*Centro de Estudos em Telecomunicações, Pontifícia Universidade Católica do Rio de Janeiro, 22452 Rio de Janeiro, RJ, Brasil

†Instituto de Física, Universidade de São Paulo CP20516, 01498 São Paulo, SP, Brasil

A deep photoluminescence emission around 1.77 eV at 77 K has been observed in annealed Si-doped $Al_{0.3}Ga_{0.7}As$ layers grown by MBE at 680 °C. It was previously suggested that this PL emission could involve the complex (Si_{As}-V_{As}) close pair[1]. PL results as a function of hydrostatic pressure could be explained either by a conduction-band to deep acceptor transition, or by a donor to deep acceptor pair recombination[2]. In the case of a band-to-acceptor transition, the complex level should be located at about 70 meV above the Si_{As} level, while in the case of a donor-to-acceptor transition the active level of the complex would be even closer to the Si_{As} level. One puzzling feature of such an assignment is the close proximity of the levels for the Si_{As} defect, isolated and in the strongly perturbed situation.

We discuss this problem, on the basis of electronic structure calculations for the three defects Si_{As}, V_{As} and (Si_{As}-V_{As}). We adopt the cluster approach within the Hartree-Fock-Roothaan LCAO formalism, through adequate semiempirical approximations. A special pseudo-atom scheme is introduced to simulate the crystalline environment.

---

[1] P. Souza and E.V.K. Rao, *Solid State Commun.* **67**, 10 (1988)

[2] K. Uchida *et al, to be presented in this Conference*

POSITRON ANNIHILATION IN ELECTRON IRRADIATED GALLIUM ARSENIDE: ATOMIC STRUCTURE AND CHARGE STATES OF THE DEFECTS

C. Corbel, P. Hautojärvi*, F. Pierre, K. Saarinen, P. Moser**

Centre d' Etudes Nucléaires de Saclay, Insitut National des Sciences et Techniques Nucléaires, 91191 Gif sur Yvette, France

*Helsinki University of Technology, Laboratory of Physics, O215O Espoo, Finland.

**Centre d'Etudes Nucléaires de Grenoble, DRF-PHS, 38O41 Grenoble Cedex, France

Positron lifetime measurements performed in semi-insulating (SI) GaAs show that acceptors are created by electron irradiation. Two types of acceptors can be separated. The first ones are vacancy-type and anneal over a very broad range of temperature between 77 K-500 K. The second ones are ion-type and anneal at high temperature above 400 K. The data show that these two types of defects are independent and do not form close pairs. We propose that both are gallium-related defects. The negative vacancy-type defects are identified with gallium vacancies which are isolated or involved in negatively charged complexes. The negative ion-type defects are identified with isolated gallium antisites.

The introduction rate of the gallium antisites is determined to be $1.8\pm0.4\ cm^{-1}$ in the fluence range (1 to 13) $10^{17}\ e^{-}cm^{-2}$ when 1.5 MeV electron irradiation is perfomed at 20 K with subsequent annealing at 77K.

In SI GaAs, positrons do not detect any annealing stage for the vacancy-type defects in the temperature range 500-650 K where other techniques like EPR or electrical measuremnts give evidence of strong recovery. The arsenic vacancy is believed to disappear in this stage via recombination with As_i interstitials. The absence of this stage in positron experiments is consistent with the positive charge state of the arsenic vacancy in SI GaAs.

In n-type GaAs it is shown that two kinds of vacancy related defects are coexisting at low temperature after electron irradiation. It is proposed that gallium vacancy or a complex involving the anneals out at about 290 K. It is proposed that the arsenic vacancy or a complex involving the arsenic vacancy anneals out at about 550 K.

DEFECTS IN InP INVESTIGATED BY POSITRON ANNIHILATION TECHNIQUE

T. BRETAGNON, S. DANNEFAER and D. KERR
Department of Physics, University of Winnipeg, Winnipeg, Manitoba R3B 2E9 Canada

The positron annihilation lifetime technique has been used successfully for a few years in the study of defects in semiconductors such as silicon and gallium arsenide. However, few results are available in the case of indium phosphide.

In this communication we present the results of a systematic study of as-grown defects in several InP crystals. The samples were n-type (undoped and S-doped), p-type (Zn-doped) and semi-insulating (Fe-doped) indium phosphide. Trapping by vacancy-like defects was observed in all of the materials. The lifetimes of trapped positrons was 271 ps, 272 ps and 267 ps for n-type, p-type and semi-insulating material respectively. Low-temperature measurements were also performed. From these results the lifetime was interpreted to arise from a neutral monovacancy defect.

In the case of semi-insulating material electron irradiation at room temperature with an energy of 2.5 MeV has also been performed. The results showed an increase of the defect lifetime from 267 ps, in unirradiated material, to 300 ps, for doses above $2 \times 10^{17} e^-/cm^2$. This result suggests the formation of vacancy complex defects such as divacancies.

ELECTRICAL AND OPTICAL PROPERTIES OF GaAs DOPED WITH Li

Haflidi P. GISLASON [1], Isak S. HAUKSSON [1], Jon T. GUDMUNDSSON [1], Margareta LINNARSSON [2] and Erik JANZÉN [3]
1 Science Institute, University of Iceland, Dunhaga 3 107 Reykjavík, Iceland.
2 Royal Institute of Technology, Box 1298, S-164 28 Kista, Sweden.
3 University of Linköping, S-581 83 Linköping, Sweden

The correlation between electrical conductivity and photoluminescence (PL) spectra of GaAs material diffused and ion-implanted with the group-I element Li has been investigated. Li diffusion is known to compensate both n- and p-type GaAs, and our starting material includes a wide range of n-type and p-type GaAs as well as semi-insulating material. Li diffusion of GaAs also has a profound effect on the PL spectra of the as-grown material. The present study examines the relation between these spectral changes and the compensation degree of the samples.

Li doping gradually reduces the intensity of the well known 1.36 eV Cu_{Ga} PL band which is usually present through inadvertent contamination of the samples during heat treatment. PL bands observed after Li doping of n-type horizontal Bridgman material include a strong band at 1.34 eV as well as bands at 1.45 and 1.48 eV [1]. The doping procedure strongly suggests that these bands are Li related, although recent reports attribute PL bands at similar spectral positions to native defects present in heat treated GaAs [2]. Careful investigation rules out this possibility in our samples.

We find that Li doping of both n- and p-type samples occurs in two stages. First, the Li gradually compensates the shallow doping until full compensation is obtained and the samples become semi-insulating. Further Li doping makes the semi-insulating samples conducting again. In both cases p-type conductivity is measured in the second stage. In order to reach Li concentration above compensation conditions, typical starting material with carrier concentration around 1×10^{17} cm^{-3} requires Li diffusion at temperatures exceeding 800 °C.

Both originally n- and p-type samples that have been converted to p-type after compensation are found to exhibit a strong PL band at 1.45 eV. Other PL bands do not consistently appear in these samples. In the paper we present a systematic study relating the Li concentration measured by secondary ion mass spectroscopy (SIMS) after Li diffusion at different temperatures between 400 and 800 °C, the corresponding compensation degree as measured by Hall measurements and the observed changes in photoluminescence spectra caused by the Li diffusion. In addition we compare these observations for GaAs diffused with Li with ion-implanted semi-insulating GaAs which underwent heat treatment at different temperatures in order to activate the implanted Li both electrically and optically.

1. H.P. Gislason, E.Ö. Sveinbjörnsson, B. Monemar, and M. Linnarsson, *Impurities, Defects and Diffusion in Semiconductors*, MRS, Pittsburgh 1990, p 127
2. Z.Q. Fang *et al*, Journal of Electronic Materials **18**, 123 (1989)

STRUCTURE OF 1.2 eV PL BAND CENTER IN GaAs:Te,Sn

N.S.AVERKIEV, A.A.GUTKIN, E.B.OSIPOV, M.A.RESHCHIKOV, V.E.SEDOV and V.R.SOSNOVSKI
A.F.Ioffe Physical-Technical Institute,
Leningrad, 194021, USSR

The wide photoluminescence (PL) band near 1.2 eV is often seen in GaAs doped with elements of II- or VI-group. It is supposed the band is due to a complex of two defects : a gallium vacancy (V_{Ga}) and a donor in the nearest site (D_{Ga} or D_{As} for II- and VI-group elements respectively). Up to now the symmetry of such complexes has been expected to be trigonal ($V_{Ga}D_{As}$) and orthorombic ($V_{Ga}D_{Ga}$) [1].

We have investigated Chochralski grown n-GaAs:Te and n-GaAs:Sn single crystals (n_0=10^{17}–10^{18} cm^{-3}) by means of excitation spectroscopy, polarized luminescence and piezospectroscopy, and have found that: (i) the symmetry of the both groups of the centers is monoclinic, (ii) the total equilibrium distortion of the center in the excited state differs from that in the ground state (it is close to distortion along ⟨111⟩ axis in the first case and along ⟨110⟩ (or ⟨001⟩) axis in the second one), (iii) the incompletely symmetric zero oscillations of the center in the excited state give rise to variations of distortion which result in spectral dependence of PL polarization.

The values of the excited levels' splittings and the deformation potential constants were estimated in terms of the developed model of the center. Such type of the center symmetry is probably due to the Jahn-Teller distortion of the gallium vacancy.

[1] E.W.Williams. Phys. Rev., 1968, v. 168, p. 922.

PN 6

Localized Vibrational Mode Resonance Raman Spectroscopy of Shallow Impurities in GaAs

T. D. Harris and J. K. Trautman, Room 1A-320, AT&T Bell Laboratories, Murray Hill, N. J. 07974

It has been recently reported that the localized vibrational mode (LVM) E1 gap resonanance Raman enhancement of shallow donors in GaAs differs substantially from that of shallow acceptors. This surprising result was obscured by the limited number of exciting energies available in the original studies. We will report the complete LVM Raman excitation profiles for group II and IV acceptors and group IV and VI donors in GaAs. The donor resonance enhancement exceeds the optical phonon enhancement by more than 10 and is reproducibly to higher energy than the published E1 energy gap. The acceptors show no enhancement greater than the optical phonon. In addition we will report on Raman spectroscopy of donor LVM for samples under hydrostatic pressures sufficient to convert shallow donors to the DX state. Comparison of these spectra with published infrared transmission measurements, including the symmetry and frequency of the DX mode versus the shallow donor mode will be included. The potential sources of the difference in acceptor and donor behavior will also be discussed.

METASTABLE STATES IN SEMI-INSULATING GaAs REVEALED BY THERMALLY STIMULATED CURRENT SPECTROSCOPY

Z-Q. FANG and D. C. LOOK
Physics Department, Wright State University
Dayton, OH 45435 USA

Native defects in undoped semi-insulating (SI) LEC-GaAs with different stoichiometries have been studied by thermally stimulated current (TSC) spectroscopy with near band-edge light ($h\nu$=1.46 eV) and infrared (IR) light ($h\nu \leq$ 1.12 eV) in conjunction with photocurrent and Hall effect measurements. 1.46 eV TSC spectra reveal, with excellent signal-to-noise, at least seven traps with energy levels of 0.49 eV (T_2), 0.42 eV (T_3), 0.29 eV (T_4), 0.27 eV (T_5), 0.23 eV ($T_5^\star$), 0.21 eV (T_6), and 0.17 eV ($T_6^\star$), respectively. Based on the trap depths, the stoichiometry dependencies and other factors the observed traps are believed to be due to point defects, such as As_{Ga}, Ga_{As}, V_{Ga}, and V_{As} or their complexes with each other and with impurities. In contrast with using 1.46 eV light, the application of IR light leads to a well-known photocurrent quenching, the magnitude and rate of which are found to be dependent on stoichiometry. TSC spectra obtained by using only a few seconds of IR excitation are basically the same as those obtained by using 1.46 eV light; we designate the basic spectrum as TSC feature I, and believe that it is associated with the normal state of EL2. However the TSC spectra taken as a function of IR photoquenching of EL2 show several drastic changes: i.e. 1) T_4, T_5, and $T_5^\star$ are largely suppressed; 2) at nearly the same time, T_2 and T_3 are fully or partially transformed into a new trap $T_2^\star$, depending on stoichiometry; 3) new traps, T_0 and T_1 are developed, especially in As-rich SI-GaAs; and 4) a strong TSC peak at $T < 90K$ is also stimulated for Ga-rich SI-GaAs samples. The final TSC spectra obtained after the complete photoquenching of EL2 are referred as TSC feature II. Hall effect measurements reveal: 1) a p-type conductivity after IR photoquenching with hole concentrations ranging from 10^{10} to 10^{11} cm^{-3}, depending on stoichiometry; 2) evidence that T_0, T_1 and $T_2^\star$ in TSC feature II are hole traps; and 3) evidence that $T_6^\star$ is probably an electron trap. For all samples, the TSC spectra can be reversibly changed from feature II back to feature I by raising the temperature to around 120K, which is exactly the same as the temperature of thermal recovery for the transformation of EL2 from its metastable state (EL2*) back to the normal state. The optical recoveries of TSC spectra from feature II to feature I were also checked by using 1.46 eV and 0.9 eV light at 90K. All data are consistent with the traps having a direct association with EL2 or EL2*, rather than an indirect association; the latter could result from a change in the dominant free carrier (being trapped) as EL2 transforms to EL2*. The simplest explanation of these phenomena is that the quenching/recovery process is controlled by one basic defect (probably As_{Ga}), and that several of the observed TSC peaks result from complexes of As_{Ga} with other defects or possibly impurities. Electron-irradiation experiments help to clarify some of these issues.

IRRADIATION-INDUCED ELECTRONIC LEVELS REMOVED IN THE 280K DEFECT-ANNEALING STAGE OF N-GaAs

W O Siyanbola, A C Irvine and D W Palmer
Physics and Astronomy Division, University of Sussex
Brighton BN1-9QH, UK

We report further results on the thermal annealing of deep electronic states associated with irradiation-induced defects that anneal near 280K in n-GaAs.

In recent previous work[1] using Capacitance-Voltage measurements at low temperature we have observed that deep electron traps produced by 1.0 MeV proton irradiation of n-GaAs at 120K are removed in thermal annealing stages near 180K, 235K and 280K. In subsequent work[2] we have found, by optical-excitation minority carrier deep level transient spectroscopy (OMCTS) on n-GaAs similarly proton-irradiated at 120K, that three irradiation-induced hole traps, at E_v+0.16eV, at and near E_v+0.25eV and at E_v+0.42eV, are removed in a thermal annealing stage near 280K. We have proposed there that the carrier traps that anneal near 280K as measured in our C-V and OMCTS experiments correspond to the defects removed in the 280K annealing stage found by Thommen[3] in studies of the annealing of electron-irradiation induced electrical-resistivity increase in n-GaAs.

We now present data on isothermal and isochronal annealing near 280K as obtained in further C-V and OMCTS measurements on n-GaAs irradiated at low temperature by protons and by helium ions. The results, showing first-order defect annealing with activation energies and pre-factors of about 0.82eV and $10^{11.5}s^{-1}$ respectively, strongly support our proposal that the three irradiation-induced electronic levels that we observe are associated with defects that anneal in the Thommen 280K stage. We find also that the broad hole trap at about E_v+0.25eV was not produced by helium-ion irradiation that caused significant lowering of the Fermi energy in the GaAs.

We discuss the possible natures of the irradiation induced defects, their production by electron- and ion-irradiations, and the annealing processes observed.

---

1. W O Siyanbola and D W Palmer, Semicond. Sci. Technol. 5 (1990) 7-15
2. W O Siyanbola and D W Palmer, Phys. Rev. Lett. 66 (1991) 56-59
3. K Thommen, Radiat. Eff. 2 (1970) 201-210

Low fluence implantations in GaAs: A Mössbauer spectroscopy investigation of individual and overlapping damage cascades

H.Andreasen, J.W.Petersen, and G.Weyer
Institute of Physics, University of Aarhus
DK 8000 Aarhus C, Denmark

The microscopic surroundings of ^{119}Sn probe atoms from the decay of implanted radioactive ^{119}In precursors in GaAs have been studied by Mössbauer spectroscopy. Fluences of ^{119}In between 10^{11} and 10^{13} atoms/cm^2 have been implanted in the temperature range 50-400K. The fluences cover the transition regime from isolated to overlapping damage cascades. Different sites have been distinguished and assigned to substitutional In, interstitial In, and In-vacancy defects. Unexpectedly strong fluence dependencies have been observed. Significant in-beam annealing is concluded in the temperature range above 200K. For low fluence ($\lesssim 10^{12}$ atoms/cm^2) destinct annealing stages have been found and the defect reaction kinetics was followed on an atomic scale. A model based on the onset of mobility of lattice defects in these stages is proposed: Ga_i and In_i are mobile at $\gtrsim$50K, V_{Ga} at 230K, and V_{Ga}-V_{As} pairs at 280K.

Optically Detected Electron-Nuclear Double Resonance of the M_s=0 State of a P_{Ga}-Y_P Spin-Triplet Center in GaP

H. J. Sun, F. C. Rong†, and G. D. Watkins
Sherman Fairchild Laboratory and Physics Department
Lehigh University, Bethlehem, PA 18015, USA

†GEO-Centers, Inc., Electronics Technology and Devices Laboratory, Fort Monmouth, NJ 07703, USA

An Optically Detected Electron-Nuclear Double Resonance (ODENDOR) study of the phosphorus antisite-related defect P_{Ga}-Y_P in GaP is presented. Observed in an excited spin triplet (S=1) state via photoluminescence at ~1.1eV, it is established that the observed ODENDOR transitions arise from the M_s=0 state. The defect serves as a model to demonstrate the unusual features of ODENDOR spectroscopy in this state for which there are no first-order magnetic hyperfine effects [1]. By extending the analysis to second and third-order perturbation, several of the important nuclear gyromagnetic-ratio and magnetic hyperfine parameters could be extracted.

Our results confirm that the core of the defect contains a phosphorus atom with three equivalent phosphorus nearest neighbors, as proposed in previous ODMR studies [2,3]. We see no ODENDOR signal that can be ascribed to an impurity (Y_P) replacing the fourth phosphorus nearest neighbor, indicating that if an impurity is there, it has no major abundant nuclear isotope with spin. This appears to rule out some of the previously-proposed defect models. Several sets of Ga ODENDOR signals are detected. We tentatively assign one of these to the three equivalent nearest neighbors to Y_P because of their large resolved quadrupole interactions. The orientation and magnitude of their quadrupole coupling tensors are consistent with the idea that Y_P could be a phosphorus vacancy. Such a defect, P_{Ga}-V_P, is an interesting possibility, the corresponding As_{Ga}-V_{As} in GaAs having been suggested previously by Baraff and Schluter [4] as a bistable partner to the V_{Ga} defect.

[1] F. C. Rong, H. J. Sun, and G. D. Watkins, Phys. Rev. B 43, XXX (1991).
[2] K. P. O'Donnell K. M. Lee, and G. D. Watkins, Solid State Commun. 44, 1015 (1982).
[3] N. Killoran, B. C. Cavenett, M. Godlewski, T. A. Kennedy, and N. D. Wilsey, J. Phys. C 15, L723 (1982).
[4] G. A. Baraff and M. Schluter, Phys. Rev. Lett. 55, 2340 (1985).

THE GALLIUM VACANCY IN p-TYPE GaAs : AN ELECTRON PARAMAGNETIC RESONANCE STUDY AND A TIGHT BINDING GREEN FUNCTION MODELIZATION.

Y.Q. Jia and H.J. von Bardeleben
Groupe de Physique des Solides,
Centre National de la Recherche Scientifique,
Université Paris 7, Tour 23, 2 Place Jussieu,
75251 Paris Cedex 05, France

D. Stievenard and C. Delerue
Laboratoire de Physique des Solides,
I.S.E.N., 41 boulevard Vauban, 59046 Lille Cedex, France.

Whereas arsenic vacancy related defects in GaAs have been studied in detail by Deep Level Transient Spectroscopy (DLTS) (1), Electron Paramagnetic Resonance (EPR) (2) and positron annihilation (PA) techniques (3), the information about the gallium vacancy related defects is still very limited. Recently, it has been shown by positron annihilation that gallium vacancy defects can be formed by electron irradiation in p-type GaAs (4).

We have undertaken a detailed EPR study on the electron irradiation induced defects in Zn doped GaAs including the dose, energy and Fermi level dependence of their introduction rate as well as their thermal stability.

We will present in particular the results concerning the dominant paramagnetic defect with spin Hamiltonian parameters $g_{\parallel} = 1.98 \pm 0.02$, $g_{\perp} = 2.08 \pm 0.01$, $A_{\parallel} = (280 \pm 20) \times 10^{-4}$ cm^{-1}, $A_{\perp} = (130 \pm 10) \times 10^{-4}$ cm^{-1}, which we attribute to the trigonally distorted gallium vacancy. The introduction rate and the Fermi level dependent thermal stability of this defect are correlated with the PA results. The attribution is confirmed by a tight binding Green's function modelization, which from the electron localization and the C_{3v} symmetry identifies this defect as the distorted V_{Ga}^{2-} vacancy.

REFERENCES

1. D. Stievenard, X. Boddaert and J.C. Bourgoin, Phys. Rev. B 34, 4048 (1986).
2. H.J. von Bardeleben and J.C. Bourgoin, Phys. Rev. B 33, 2890 (1986).
3. C. Corbel, M. Stucky, P. Hautojarvi, K. Saarinen and P. Moser, Phys. Rev. B 38, 8192 (1988).
4. F. Pierre, Ph.D. Thesis, Université Paris XI (1989).

HIGH TEMPERATURE NMR STUDY OF INTRINSIC DEFECTS IN GaAs

Wei-Min HAN, John A. GARDNER, and William W. WARREN, JR
Department of Physics, Weniger Hall 301, Oregon State University, Corvallis, OR 97331-6507

We have measured the ^{69,71}Ga and ^{75}As nuclear spin relaxation rates in GaAs between room temperature and 1000 °C. The samples consisted of powdered commercial semi-insulating GaAs sealed in small evacuated quartz capsules. In order to vary the stoichiometry, some cells contained excess Ga or As and were heated to temperatures in excess of 1100 °C for several hours before initiating measurements. The nuclear relaxation rates were measured by standard pulsed NMR methods at a frequency of 11.4 MHz.

The spin-lattice relaxation rates $1/T_1$ in all samples exhibited evidence of two distinct relaxation processes. The first, dominant below about 600 °C, increases with temperature approximately as T^2 and is attributed to electric quadrupcle relaxation via thermal phonons.[1,2] At higher temperatures, the relaxation is dominated by a second process which is distinguished by a much stronger temperature dependence. The temperature dependence in this range is consistent with a thermally activated process. We attribute the high temperature process to electric quadrupole interactions with diffusing defects. These are likely to be thermally generated As vacancies, although we are unable to conclude this from the present data.

Surprisingly, we observed virtually no effects from our attempts to introduce excess Ga and As into the semi-insulating material. This suggests that the vacancy concentrations associated with non-stoichiometry are small compared with the defect concentrations present in nominally stoichiometric material at high temperature. The implications of these results for the solubility of excess Ga and As at high temperatures will be discussed.

1. R. L. Mieher, Phys. Rev. 125, 1537 (1962)
2. J. A. McNeil and W. G. Clark, Phys. Rev. B 13, 4705 (1976)

Effects of Isovalent Impurity Doping on Stoichoimetry and Defects in III - Y Semiconductors.

Yu.V.Shmartsev
A.F.Ioffe Physico-Technical Institute, Academy of Sciences of the USSR, 194021 Leningrad, K-21, USSR

By isovalent impurity one usually understands impurity whose atom has the same outer electron shell structure as the host lattice atom substituted by it. It is known that isovalent impurities do not create local (extrinsic) states in the gap, at least in direct band gap semiconductors.

Nevertheless, isovalent impurity doping of direct-gap III-Y semiconductors produces a strong impact on their mechanical, electrical and optical properties. Isovalent impurity doping has recently permitted obtaining

- semi insulating bulk crystals and epitaxial GaAs films with a low dislocation density;
- epitaxial GaAs and GaSb films with a low residual impurity and intrinsic lattice defect concentration;
- epitaxial GaAs and AlGaAs films with a low concentration of deep impurity levels.

Experimental investigation of the effect of the isovalent impurities In, Ga, Sb, Bi on the electrical and optical properties of III-Y semiconductors (GaAs, InP, GaSb) permitted us to reveal the main mechanisms responsible for the change in these properties as a fun,tion of the type and concentration of the isovalent impurity involved. One can conclude that isovalent doping permits one to control the structure of defects produced in semiconducting crystals and layers and through it their mechanical, electrical and optical properties.

Session PO

Hydrogen in Compound Semiconductors

Wednesday Evening, 24 July

Rathbone Hall

SHALLOW AND DEEP RADIATIVE LEVELS OF H COMPLEXES IN GaAs

M. CAPIZZI, C. COLUZZA, Valentina EMILIANI, P. FRANKL,
A. FROVA, and Francesca SARTO
Dipartimento di Fisica, Università di Roma "La Sapienza", 00185 Rome, Italy

Direct observation of an optically active hydrogen-induced deep level - seen through a transition at ~1.15 eV in GaAs - is achieved by liquid nitrogen temperature photoluminescence experiments. The material, grown by MBE, is nonintentionally doped p-type; hydrogenation up to high densities is achieved by low-energy ion irradiation from a Kaufman source. A corresponding state at 1.37 eV is seen in the MBE-GaAlAs capping layer. The results were confirmed by study of differently grown material, e. g. by liquid encapsulation and liquid phase epitaxy.

In the limit of the highest H concentrations attained (total dose reaching the surface above 10^{18} atoms/cm^2), radiative recombination via the deep level becomes remarkably efficient, so as to shorten the carrier lifetime by orders of magnitude - as proven by time resolved measurements in the excitonic region (where, of course, all transitions become sharply attenuated).

This behavior, consistently with theoretical speculations, is ascribed to the creation of a deep acceptor for H bound to arsenic in antibonding position. The emission intensity and spectral lineshape, as well as their evolution with raising temperature, are well explained in terms of an "internal" transition to the deep level from a shallow donor, itself a result of hydrogenation (see below). The observed behavior is remarkably similar to that known for the Ga-vacancy/donor complex and explained in terms of the configurational-coordinate model.

At moderately lower H-doses, i. e. prior to the insurgence of the newly observed emission band, the present data confirm the known beneficial effect of defect center passivation, with enhancement of most original emission lines (e. g. free exciton). At liquid helium, an optimal condition is reached for a dose of ~ 10^{17} H atoms/cm^2, then the effect of lifetime dropping takes over.

It is in this same dose-range, that the H-induced shallow levels are clearly visible in the form of a D-A like emission band, absent in the virgin sample (which is virtually donor-free). This band falls about 60 meV below the bandgap and corresponds to donor and acceptor levels both of about 30 meV, conceivably generated by the lattice distortion in the surroundings of H, any time it binds to defects, impurities or lattice atoms.

DISSOCIATION KINETICS OF HYDROGEN-NEUTRALIZED Si DONORS AND DX CENTERS IN GaAs AND AlGaAs

G. ROOS*†, N. M. JOHNSON*, C. HERRING*‡, and J. S. HARRIS†
*Xerox Palo Alto Research Center, Palo Alto, CA 94304, USA
†Department of Electrical Engineering, Stanford University, Stanford, CA 94305, USA
‡Department of Applied Physics, Stanford University, Stanford, CA 94305, USA

The stability of hydrogen-impurity complexes in semiconductors is of fundamental interest because it relates to the binding energy of the complex and the activation energy for hydrogen migration, and both of these quantities depend on the charge states of the dissociation products. The apparently greater thermal stability of such complexes in III-V, as compared to elemental, semiconductors has stimulated technological interest which provides added incentive to understand the fundamental processes.

This paper presents results from a study of the thermal dissociation kinetics of hydrogen-dopant complexes in *n*-type GaAs:Si and MBE-grown $Al_xGa_{1-x}As$:Si ($x<0.35$). In the alloy both hydrogen-neutralized Si donors and DX centers were examined. Specimens were exposed to monatomic hydrogen from a remote hydrogen plasma, and dopant neutralization was readily achieved in the temperature range of 225-300°C to depths near 0.3 µm for $\sim1\times10^{17}$ Si/cm^3. Previous studies leave unresolved questions concerning the competition between the dissociation of Si-H complexes and their re-formation. To minimize ambiguities of interpretation, the thermal dissociation kinetics were determined within the space charge layer of reverse biased Schottky-barrier diodes. The advantage of this approach is that complex re-formation is minimized within the space charge layer because dissociated H^- or H^+ would drift away, and re-formation from H^0 or H^+ could well require free carriers. Depth redistribution of the complex thus provides information on the charge state of the migrating hydrogen. The technique has been previously used to determine dissociation energies and product charge states for H-dopant complexes in silicon.

Reactivation of Si donors was recorded with C-V measurements, and recovery of DX centers was monitored with both C-V and DLTS. The thermal dissociation times yielded dissociation energies of the complexes. For example, for the Si donor in GaAs an Arrhenius analysis yields a dissociation activation energy of 1.2 ± 0.1 eV, which is significantly smaller than previous determinations. Both the redistribution of the complex and reactivation of neutralized donors in the field-free region suggest that H^- is a dissociation product. Thus, from the electrical results (supplemented with SIMS data) we can propose a model for the reaction kinetics and product charge states of Si-H complexes in *n*-type GaAs and AlGaAs.

Equilibrium sites and relative stability of atomic and molecular Hydrogen in GaAs

L. Pavesi[1] and P. Giannozzi[2]

[1] Physics Departement, University of Trento, I-38050 POVO (TN) Italy

[2] IRRMA, PH-Ecublens, CH-1015 Lausanne, Switzerland

Hydrogen (H) diffusion into semiconductors could be used as a post growth technique for improving the optical and electrical properties of these materials. For H in Si, detailed first principle calculations have been done while for H in GaAs, a great deal of experimental results has been accumulated, but only few theoretical works have been published. For this reason we have undertaken an investigation of the behavior of hydrogen in GaAs. We have studied different charge states (H^+, H^- and H^o) of the impurity, the formation of H_2 molecule and the H_2^* defect. We have used the *ab-initio* Local Density–pseudopotential scheme with large supercells (up to 32 atom). We have allowed for full lattice relaxation.

The lowest energy state turns out to be the H_2 molecule in a tetrahedal position (T site), where it finds a global *minimum*. Another interesting structure is the so called H_2^* complex formed by one hydrogen in the bond center (BC) site and one hydrogen in a T site. This defect has an energy 1 eV higher than the H_2 molecule in the T site.

Although energetically less favoured atomic hydrogen is experimentally observed. Thus we compute the stable charge state of H as a function of the Fermi energy (μ). If μ is at the bottom of the conduction band, the stable state is H^-. For n-doped GaAs, H^- diffuses in the low valence charge density region and the passivation of dopant atoms results from neutralization which follows the pairing between hydrogen and the impurity. If μ is at the top of the valence band, the stable charge state is H^+ in the BC site. A diffusive path for H^+ is found between the BC through high valence charge region. In these sites H^+ induces the formation of a deep donor level and the acceptor neutralization follows a bond rearrangement as H gets into the bond. Our results indicate that hydrogen in GaAs forms a negative-U system. The sequence of equilibrium states is H^+ followed by H^- as the Fermi energy is raised, while H^o is never the stable state of lowest energy. Finally, we present a comparison with the theoretical results for other semiconductors and with the experimental results for GaAs.

UNINTENTIONAL HYDROGENATION OF III-V SEMICONDUCTORS DURING DEVICE PROCESSING

S. J. Pearton+, C. R. Abernathy+, W. S. Hobson+, U. K. Chakrabarti+, D. M. Kozuch* and M. Stavola*
+AT&T Bell Laboratories, Murray Hill, NJ 07974 USA
*Lehigh University, Bethlehem, PA 18015 USA

Atomic hydrogen is shown to be incorporated into III-V semiconductors such as GaAs, AlGaAs and InP during a number of device fabrication steps. Hydrogen injection into p-type GaAs during boiling in water or etching in H_2SO_4:H_2O_2:H_2O has been detected by the resultant acceptor passivation and more directly by secondary ion mass spectrometry after processing with deuterated chemicals. Similar hydrogen injection into InP was observed after boiling in D_2O. Dry etching of the III-V semiconductors in CH_4/H_2 or CH_3Cl plasmas leads to substantial dopant passivation in GaAs, AlGaAs, InP InGaAs and multi-layers of these materials. Similar passivation can occur even when hydrogen is not a specific part of the plasma chemistry, due to the presence of water vapor, photoresist mask erosion and so on. Hydrogen also readily permeates into the III-V's during annealing at moderate temperatures (~500°C) in H_2 ambients. This has been shown previously for bulk n- and p-type GaAs, but even more dramatic results are obtained using degenerately carbon-doped epitaxial layers. Finally, it is shown that gas-source growth methods such as Metal Organic Molecular Beam Epitaxy and Metal Organic Chemical Vapor Deposition produce layers containing significant concentrations of hydrogen originating from the source chemicals. Although the hydrogen concentration is obviously a function of the growth parameters, we show it is closely correlated with the doping type and density in the epitaxial layer.

Hydrogen Passivation of Shallow and Deep Centers in GaSb

A. Y. Polyakov[1], S. J. Pearton[2], R. G. Wilson[3], P. Rai-Choudhury[4], R. J. Hillard[4], X. Y. Bao[1], M. Stam[1], A. G. Milnes[1] and T. E. Schlesinger[1]

1. Department of Electrical and Computer Engineering, Carnegie Mellon University, Pittsburgh, PA 15213-3890
2. AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, NJ 07974-2070
3. Hughes Research Laboratories, 250 MS RL 56, 3011 Malibu Canyon Rd., Malibu, CA 90265
4. Solid State Measurements, Inc., 110 Technology Drive, Pittsburgh, PA 15275

Hydrogen passivation experiments on n- and p-type GaSb will be reported. The samples were deuterium treated at 200 and 250°C. After deuterium treatment SIMS profiling, two probe resistivity profiling, photoluminescence and DLTS measurements were done. Hydrogen behavior in GaSb is shown to be similar to that of InP, i.e. significant passivation of acceptors is detected whereas donors are passivated only slightly (approximately 2 times decrease in a material with $n=2x10^{17}cm^{-3}$). Hydrogen diffusivity is shown to be faster in p-GaSb than in n-GaSb with comparable dopant concentrations. In p-n junctions hydrogen is confined to the p-type region and its concentration drops sharply as it moves to the n-type region. As the concentration of acceptors increases the penetration depth of hydrogen goes down.

The influence of hydrogen on deep centers as evidenced by DLTS and PL measurements will also be reported.

HYDROGEN IN InAs ON GaAs HETEROSTRUCTURES: DIFFUSION BEHAVIOR, ELECTRICAL AND OPTICAL EFFECTS.

B.THEYS(a), S.KALEM(b)[1], A.LUSSON(a), J.CHEVALLIER(a), C.GRATTEPAIN(a), M. STUTZMANN(c).
(a) Laboratoire de Physique des Solides de Bellevue, CNRS, 92195 MEUDON (France)
(b) Coordinated Science Laboratory. University of Illinois at Urbana Champaign, URBANA, IL 61801 (USA)
(c) Max Planck Institut für Festkörperforschung 7000 STUTTGART 80 (Germany)

Non-intentionally doped InAs layers grown by molecular beam epitaxy on GaAs substrates have been exposed to a hydrogen plasma in order to get hydrogen diffusion. SIMS measurements show that the diffusion coefficient of hydrogen is much higher in these materials than in InAs on InAs layers or in bulk InAs.

The electrical properties of these InAs on GaAs layers are strongly influenced by the presence of hydrogen. Resistitivy and Hall effect measurements show that the free electron concentration increases by one order of magnitude after hydrogenation.

Simultaneously, the optical properties of these layers are also modified. The near-band-edge photoluminescence spectrum is altered and in the far infrared reflectivity spectrum the plasma edge minimum is shifted towards higher wavenumbers. That is consistent with the increase of the free electron concentration. On the other hand, the infrared optical reflectivity of InAs on InAs layers or bulk InAs does not change under hydrogenation.

All these results suggest that the presence of misfit dislocations in the InAs on GaAs epilayers plays a role in the observed effects. A model based on the hydrogen passivation of electronic state related to dislocations is proposed to explain the changes of the properties of the InAs on GaAs layers under hydrogenation.

1. Present address: Center for Advanced Electronics Materials, North Carolina State University, RALEIGH NC 27695 (USA).

Session PP

Metal Impurities in Compound Semiconductors

Wednesday Evening, 24 July

Rathbone Hall

ELECTRICAL PROPERTIES OF Yb, Er DOPED InP

Djelloul SEGHIER, Taha BENYATTOU, Georges BREMOND, Frédérique DUCROQUET and Gérard GUILLOT
INSA de Lyon, Bât.502, LPM (associé au CNRS), 20 Av. Albert Einstein, 69621 Villeurbanne Cédex, France

Christophe LOHMER, Bertrand LAMBERT, Yves TOUDIC and Alain LE CORRE
CNET/LAB/OMC/MPA, 22301 Lannion, France

Rare earths (REs) are well known for their optical properties. The 4f electrons give rise to transitions which are very sharp and almost insensitive to the crystal field. These properties are very interesting in view of realizing new optoelectronic devices based on REs doped III-V materials since it has been shown that the REs luminescence can be excited electrically.

However, there is a poor knowledge of the electrical activity of this kind of impurity. Recent works have reported that ytterbium ions act as an acceptor near the conduction band in InP [1].

We present results from capacitance spectroscopy experiments on Yb and Er doped InP. We have found that for n type InP:Yb ions introduce a level at 10 meV below the conduction band (CB). In p-type material a hole trap at 50 meV from the valence band (VB) has been detected. EPR studies made on InP:Yb have shown that the detected level is not related to the Yb^{2+}/Yb^{3+} level [2]. From these results, we conclude that ytterbium ions act as an isovalent trap in InP and introduce an electron and a hole trap due to a local potential related to the REs. This potential could be induced by a distortion of the crystal lattice caused by the large REs ionic radius.

In the case of n-type Er doped InP, no electrical activity has been detected leading to an upper limit of electrically active erbium ions of 0.05 %.

In conclusion, we have shown that Yb ions introduced two levels in InP at 10 meV from CB and 50 meV from VB. No evidence of an electrical activity was found for Er doped InP. This could be explained by the low erbium ion solubility in InP leading to the formation of complexes.

This work was supported by CNET Lannion under contract n° 90.8B.006 LAB.

References

1. P.S. WITHNEY, K. UWAI, H. NAKAGOME and K. TAKAHEI, J. Appl.Phys. 61, 4877 (1987)
2. B. LAMBERT, Y. TOUDIC, G. GRANDPIERRE, A. RUPERT and A. LE CORRE, Electron.Lett. 28, 1458 (1988)

ELECTRON PARAMAGNETIC RESONANCE IDENTIFICATION OF A TRIGONAL Fe-S PAIR IN GaP

J. Kreissl, W. Ulrici* and W. Gehlhoff
Zentrum fürWissenschaftlichen Gerätebau,
Rudower Chaussee 6,D/O-1199 Berlin, FRG
*Zentralinstitut für Elektronenphysik,
Hausvogteiplatz 5/7, D/O-1086 Berlin, FRG

Transition metal (TM) defects in III-V semiconductors have gained considerable interest where most of the activities were focussed onisolated TM with a $3d^n$ configuration. The knowledge about the spatial and electronic structure of associates or complexes of TM is not very complete. An important group within the known complexes are the pairs between TM acceptors and shallow group VI donors. In GaP such pairs of Ni and Mn have been identified by optical studies and EPR.
Recently two different Cr-related pairs were reported by us: A Cr^{+}_{Ga}-S_P pair of trigonal symmetry in n-type GaP:Cr:S and a $Cr^{3}_{Ga}{}^{+}$-Zn_{Ga} pair of monoclinic symmetry in p-type GaP:Cr:Zn. The latter one was the first observation of a pair defect with a TM acting as a donor. In all cases the donor-acceptor pairing by Coulomb attraction is responsible for their formation.
In this paper we report EPR experiments on GaP:Fe:S and GaP:Fe:Zn carried out to identify Fe-related donor- acceptor pairs.
In n-type GaP:Fe:S a strongly angular dependent EPR spectrum is observed indicating a centre of trigonal symmetry. The angular dependence of the fine structure transitions can be explained by $S=3/2$. In the case of the used X band microwave energy the Zeeman splitting and the splitting due to the trigonal crystal field are of the same magnitude (intermediate case). This requires an exact diagonalization of the energy matrix of the spin Hamiltonian. By fitting its parameter $g_{\perp}$, $g_{\parallel}$ and D are determined. The characteristic shift of the g-values evidences that the spectrum is due to $Fe^{+}_{Ga}(A^{2-})$. The strong trigonal crystal field component is caused by a spin-satisfied $S^{6}_{P}{}^{+}(A^{+})$ on nearest P site. Therefore, by the complete analysis of the EPR spectrum a Fe^{+}_{Ga}-S_P pair is identified.
In GaP:Fe:Zn only the spectrum of isolated $Fe^{3}_{Ga}{}^{+}$ was measured and no spectrum due to a Fe-Zn pair was detectable. This confirms the absence of a $Fe^{3}_{Ga}{}^{+}/Fe^{4}_{Ga}{}^{+}$ donor level in the gap of GaP and that the donor state, $TM^{4}_{Ga}{}^{+}$, is required for the formation of a TM_{Ga}-Zn_{Ga} pair.

Optically Detected Cyclotron Resonance Studies of Erbium and Ytterbium doped InP

M. GODLEWSKI
Institute of Physics, Polish Academy of Sciences
02-668 Warsaw, Al. Lotników 32/46, Poland

and

B.J. HEIJMINK LIESERT, T. GREGORKIEWICZ and C.A.J. AMMERLAAN
Natuurkundig Laboratorium, Universiteit van Amsterdam
Valckenierstraat 65, NL-1018 XE Amsterdam, The Netherlands

Recently a new excitation mechanism of rare earth (RE) intra-shell emissions was proposed. It includes binding of an exciton by a RE impurity. In this paper we verify this suggestion by a new experimental approach.

The Optically Detected Cyclotron Resonance (ODCR) method has been applied to the studies of recombination processes in semiconductors. Microwave heated free carriers may affect profoundly optical properties of the material. The first application of this method to the studies of RE-related excitation and recombination processes is presented here.

The ODCR results for Er doped InP are presented. Our results do not confirm recent suggestions on the excitonic recombination mechanism in this case. The only effect of microwaves here may be related to Joule heating of the lattice.

The ODCR studies of Yb doped InP allow to verify the excitonic mechanism of 4f-shell excitation. We prove that the Yb^{3+} intra-shell emission is induced by non-radiative recombination of Yb bound excitons due to an impurity Auger effect. The energy transfer mechanism from shallow donor - acceptor pairs to Yb is proved to be inefficient. The main effect of hot carriers on Yb emission is related to impact ionization of impurity bound excitons and shallow donors, which enhances free carrier recombination via Yb.

We prove, thus, that the excitonic excitation mechanism is certainly possible and, for some RE ions, may be a dominant one.

REINVESTIGATION OF THE OPTICAL PROPERTIES OF THE IRON IMPURITY IN GaAs AND InP

A. M. HENNEL, A. WYSMOŁEK, R. BOZEK
Institute of Experimental Physics,
Warsaw University,
Hoza 69, 00-681 Warsaw, Poland

and

D. COTE, C. NAUD
Acoustique et Optique de la Matière Condensée
Université Pierre et Marie Curie, Boite 86
F-75252 Paris, cedex 05, France

Fourier transform absorption spectroscopy measurements in the range 2 700-10 000 cm^{-1} of iron doped semi-insulating GaAs and InP are reported.

Both "excitonic" and band to level photoionization transitions, already reported in the InP case,[1] are observed in GaAs as well. These results allow the position of the iron acceptor level to be determined with "spectroscopic" accuracy and provide informations about the spin-orbit splitting of the $^5T_2$ excited state of $Fe^{2+}(3d^6)$.

The higher energy structure in InP corresponds to the beginning of a Fe-related luminescence band.[2] This suggests a new interpretation of this luminescence band.

1 A. Juhl, A. Hoffmann, D. Bimberg, and H.J. Schulz, Appl. Phys. Lett. 50, 1292 (1987)
2 L. Eaves, A.W. Smith, M.S. Skolnick, and B. Cockayne, J. Appl. Phys. 53, 4955 (1982)

Photoluminescent Properties of Yb Doped InAsP Alloys

A. J. Neuhalfen, D. M. Williams and B. W. Wessels
Department of Materials Science and Engineering
Northwestern University, Evanston, IL 60208

The photoluminescent properties of ytterbium-doped $InAs_xP_{1-x}$ were investigated. Doped alloys with compositions ranging from x = 0 to 0.17 were prepared using organometallic vapor phase epitaxy. Strong luminescence with a transition energy of 1.225 eV is observed that is attributed to intra-4f transitions of Yb^{3+} in a substitutional In-site. The emission energy of the luminescence was found to be independent of the alloy composition. However, the peak width increased slightly as a result of alloying. Some splitting of the main peak was observed. In addition, for an alloy with x=0.15 and a bandgap of 1.25 eV, an enhancement in the Yb intra-4f emission was noted. This enhancement is attributed to a resonance effect. The enhancement presumably results from either enhanced carrier transfer from the semiconductor carrier continuum to the discrete Yb levels, or through optical pumping by the photons generated by the bandgap emission.

To determine the detailed recombination mechanisms, the temperature dependence of the characteristic photoluminescence was studied for Yb doped InP and InAsP. Temperature dependent quenching of the characteristic emission was observed. The temperature at which quenching occurred depended on alloy composition. From the experiments, a model for the luminescnece quenching was developed. In the proposed model, the quenching of the Yb related intracenter transition occurs at a temperature at which the energy level of the excited state of the center becomes resonant with the bandedge. The implications of this model for asignment of ground state level of the Yb ions in InAsP will be discussed.

Session PQ

EL2

Wednesday Evening, 24 July

Rathbone Hall

ENERGY LEVEL ASSOCIATED WITH THE METASTABLE STATE OF EL2

B. Brémond, G. Guillot, R. Azoulay
Laboratoire de Physique de la Matière,
I.N.S.A., 20 avenue A. Einstein, Villeurbanne, France

D. Stiévenard, C. Delerue
Laboratoire de Physique des Solides,
I.S.E.N., 41 boulevard Vauban, 59046 Lille, France

S.L. Feng, M. Zazoui, H.J. von Bardeleben and J.C. Bourgoin
Groupe de Physique des Solides de l'Université Paris VII,
Centre National de la Recherche Scientifique,
Tour 23, 2 place Jussieu, 75251 Paris Cedex 05, France

Search for the energy level associated with the metastable state of EL2 has been undertaken in 10^{16} cm^{-3} n-type doped GaAs under hydrostatic pressure and in GaAlAs alloys of various Al composition x. A level is indeed detected by DLTS, emerging from the conduction band with increasing x or pressure, after illumination at low temperature whose thermal behavior follows the one of the metastable state. It is typically ~ 18 meV for x ~ 5 % in GaAlAs and ~ 11 meV for 6 kbars in GaAs. The emission rate is strongly sensitive to the electric field. In addition, we observed a new level associated with the stable state of EL2, which we attribute to the -/0 transition, located at 49 meV below the conduction band.

EL2 RELATED COMPLEX DEFECTS IN SEMI-INSULATING GaAs

U. Desnica and D. Desnica

Ruđer Bošković Institute, P.O.Box 1016, 41001 Zagreb, Yugoslavia

Processes induced by below-the-gap illumination and related to defects having deep levels in Liquid Encapsulated Czochralski semi-insulating GaAs crystals were studied. It has been reported recently(1) that the dynamics of both optical quenching and thermal recovery (above 125 K) of six deep-trap-related Thermally Stimulated Current signals was exactly the same as that of the EL2-related photoconductivity signal. Analysis of these results gives evidence that some of observed deep traps in GaAs are complex defects, which include, as their constituent, the EL2 defect. It means that EL2 can serve as a gettering center for other native defects and/or impurities.

The proposed model is in accordance with other recently published results connecting several deep traps (EL6, EL3, EL5 and EL14) with EL2.

(1) U.V. Desnica, Dunja I. Desnica and B. Šantić,
Appl. Phys. Lett. 58, 278 (1991)

RE-EXAMINATION OF THE CONFIGURATION COORDINATE DIAGRAM OF EL2

D.GOGUENHEIM , D.STIEVENARD
Laboratoire d'Etudes des Surfaces et Interfaces
ISEN, 41 Bd. Vauban, 59046 Lille cedex, FRANCE

G.GUILLOT
Laboratoire de Physique de la Matière
INSA Lyon, 20 Av.A.Einstein, 69621 Villeurbanne cedex, FRANCE

A detailed examination of the set of experimental electronic and optical properties of EL2 leads to the impossibility to build a self-consistent Configuration Coordinate Diagram of this defect in a classical way.[1] Indeed, the main contradiction actually lies in the difference between the classical expression of the barrier for electron capture $E_b = \frac{(E_t - S\hbar\omega)^2}{4\,S\hbar\omega}$ (>0.7 eV if one considers the experimental reported values of the thermal ionization energy E_t and of the Franck-Condon shift $S\hbar\omega$) and the experimentally observed one E_b^* (<0.1 eV). In spite of this, we have performed an accurate study of the temperature dependence of the electron emission and capture rates over a large temperature scale, showing that the capture cross section does follow the law $\sigma_\infty e^{-E_b^*/kT}$ over the whole 300-400 K range, i.e confirming the previous works. So, to remove this apparent contradiction, we have analysed the Configuration Coordinate Diagram. First, on the basis of a more complete theory of carrier capture assisted by phonons[2] assuming a single force constant k for both charge states, we prove that the conditions of validity required to get the classical expression for E_b are not satisfied in the case of EL2. At last, we can explain the discrepancy between E_b and E_b^* by a variation of the force constant k with the charge state of EL2.

[1] A.CHANTRE, G.VINCENT, D.BOIS Phys.Rev. B23, 5335 (1981)
[2] D.GOGUENHEIM, M.LANNOO J.Appl.Phys. 68 (3), 1059 (1990)

VACANCY IN THE METASTABLE STATE OF THE EL2 DEFECT IN GaAs

P. HAUTOJÄRVI, K. SAARINEN, and L. LISZKAY
Laboratory of Physics, Helsinki University of Technology,
02150 Espoo, Finland

C. CORBEL, and C. LeBERRE
Institut National des Sciences et Techniques
Nucléaires, Centre d'Etudes Nucléaires de Saclay
91191 Gif-sur-Yvette, Cedex, France

R. KRAUSE
Department of Physics, Martin-Luther University,
P.O.Box 4020 Halle, F.R. Germany

Positron annihilation experiments have been performed in semi-insulating GaAs to study the EL2 defect. Samples were LEC grown crystals obtained from various sources. After EL2 is transformed into metastable state, we observe increases both in positron lifetime and the line-shape parameter of the 511 keV radiation. The increased values of the positron parameters are stable as long as the metastable state of EL2 is retained. The positron parameters recover thermally at 120 K and optically under 1.4 eV photon illumination at 80 K in perfect correspondence with the $EL2^* \rightarrow EL2$ transformation.

The increase of positron parameters is due to positron trapping at a defect with lifetime of 255 ± 8 ps. This lifetime value is characteristic to native and irradiation-induced monovacancies in GaAs. Positron trapping at this monovacancy is strongly temperature dependent indicating that the monovacancy is negatively charged.

The conclusion from the experiments is that negative monovacancies appears after EL2 is transformed into the metastable state. The concentration of the monovacancy is higher at higher EL2 concentrations. We suggest that the structure of the metastable state of the EL2 defect involves a negative monovacancy.

FIRST-PRINCIPLES CALCULATION OF THE PRESSURE DEPENDENCE OF THE TRANSITION STATE OF EL2

C. Ziegler and U. Scherz

Institut für Theoretische Physik, Technische Universität Berlin
Hardenbergstr.36, W-1000 Berlin 12, Germany

The atomic structure and the mechanism of metastability of the EL2 center in GaAs is still discussed controversially. The mechanism of metastability has been explained by a structural transition of an isolated As-antisite to a defect pair consisting of a Ga-vacancy and an As-interstitial [1], [2]. To get further insight into the structure of EL2, we calculated the volume dependence of the $\epsilon(0|+)$ transition state of the As-antisite and compared it with pressure dependent DLTS of EL2 in its stable state.

The calculations were carried out with the self-consistent Green function technique in the framework of density functional theory within the local density approximation. We used norm-conserving nonlocal pseudopotentials and described the defect properties with basis functions centered at the defect and its four nearest neighbours. Our results were calculated by neglecting lattice relaxation and lattice vibrations.

The transition state $\epsilon(0|+)$ is the difference between the bandgap at the Γ-point E^Γ and the deep level $E(1.5)$ of the As-antisite in the energy gap: $\epsilon(0|+) = E^\Gamma - E(1.5)$. According to the Janak-Slater theorem the deep level was occupied with 1.5 electrons. It was taken with respect to the top of the valence band. Calculating the corresponding energies for different lattice parameters, we obtained the volume dependence of the transition state of the As-antisite. Like in similar LDA calculations the absolute value of the band gap at the experimental lattice parameter is too low compared with experiment. Nevertheless, the volume dependence of the band gaps at the Γ-, X- and L-point are correct with respect to the experimental values.

It has been shown by DLTS [3], [4] and [5], that the activation energy E^e of the electron emission rate of EL2 in its stable state is pressure dependent. Together with photoconductivity measurements of the pressure dependence of the activation energy of electron capture E^c [6], the experimental pressure dependence of the EL2 transition state was determined by $d\epsilon(0|+)/dp = dE^e/dp - dE^c/dp$. Using the experimental bulk modulus B, we obtained the experimental volume dependence of the transition state of EL2 given by $V\,d\epsilon(0|+)/dV = B\,d\epsilon(0|+)/dp$ and we found: 7.0 eV [3], 6.56 eV [4] and 6.33 eV [5]. Comparing these experimental results of EL2 with our theoretical value $V\,d\epsilon(0|+)/dV = 6.69\,\mathrm{eV}$ for the As-antisite we conclude that the isolated As-antisite model also holds for the pressure dependent DLTS measurements of EL2 in its stable state. But we cannot exclude the possibility of weakly interacting other defects at a distance of the second nearest neighbours or farther.

[1] J. Dabrowski and M. Scheffler, *Phys. Rev. Lett.* 60, 2183 (1988), *Phys. Rev. B* 40, 10391 (1989).
[2] D.J. Chadi and K.J. Chang, *Phys. Rev. Lett.* 60, 2187 (1988).
[3] L.Dobaczewski and A. Sienkiewicz, *Acta Phys. Pol.* A71, 341 (1987).
[4] A. Zylbersztejn, R.H. Wallis and J.M. Besson, *Appl. Phys. Lett.* 32, 764 (1978).
[5] O. Kumagai, K. Wünstel and W. Jantsch, *Sol. State Comm.* 41, 89 (1982).
[6] P. Dreszer and M. Baj, *Acta Phys. Pol.* A73, 219 (1988).

Index